Mathematisches Forschungsinstitut Oberwolfach

Mathematical Methods in Quantum Chemistry

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ABSTRACT. The field of quantum chemistry is concerned with the analysis and simulation of chemical phenomena on the basis of the fundamental equations of quantum mechanics. Since the 'exact' electronic Schrödinger equation for a molecule with N electrons is a partial differential equation in $3N$ dimension, direct discretization of each coordinate direction into K gridpoints yields K^{3N} gridpoints. Thus a single Carbon atom ($N = 6$) on a coarse ten point grid in each direction ($K = 10$) already has a prohibitive 10^{18} degrees of freedom. Hence quantum chemical simulations require highly sophisticated model-reduction, approximation, and simulation techniques.

The workshop brought together quantum chemists and the emerging and fast growing community of mathematicians working in the area, to assess recent advances and discuss long term prospects regarding the overarching challenges of
  (1) developing accurate reduced models at moderate computational cost,
  (2) developing more systematic ways to understand and exploit the multi-scale nature of quantum chemistry problems.
Topics of the workshop included:
  • wave function based electronic structure methods,
  • density functional theory, and
  • quantum molecular dynamics.
Within these central and well established areas of quantum chemistry, the workshop focused on recent conceptual ideas and (where available) emerging mathematical results.

Introduction by the Organisers

The field of quantum chemistry is concerned with the analysis and simulation of chemical phenomena on the basis of the fundamental equations of quantum mechanics. While mathematical thinking (by physicists and chemists) has always played a large role in this field, in the past years a growing and very active community of mathematicians working in the area has also emerged. The workshop was interdisciplinary, bringing together quantum chemists and mathematicians to assess the state of the art and discuss recent conceptual ideas and emerging mathematical results.

The Oberwolfach institute and format (of fewer talks than standard conferences) provided an ideal venue. It stimulated not just lively discussions (by no means limited to the explicit 10-minutes discussion slot allocated after each morning lecture). The Oberwolfach format also proved a fertile ground for cultural cross-fertilization. A clear proof that the latter was taking place was that by Wednesday morning, the first quantum chemist (Alexander Auer) was ready to spontaneously give up his planned laptop presentation for a blackboard talk.

Recurring themes of the meeting were (1) the continuing search for accurate computational methods with feasible computational cost, (2) the need for developing more systematic ways to understand and exploit the multiscale nature of quantum chemical systems, (3) new examples of quasi-exactly soluble many-electron systems.

As regards theme (1), the 'exact' electronic Schrödinger equation for an atom or molecule with N electrons is a partial differential equation in $3N$ dimensions, so direct discretization of each coordinate direction into K gridpoints yields K^{3N} gridpoints; thus the unreduced equation for a single Carbon atom ($N = 6$) on a coarse ten point grid in each direction ($K = 10$) already has a prohibitive 10^{18} degrees of freedom. The computational cost of the best wave function based methods, such as multiply-excited Configuration-Interaction methods or Coupled Cluster theory, while no longer exponential, still scales like an unphysically steep power of the particle number. By contrast, density functional theory, which replaces the linear many-electron Schrödinger equation in $3N$ dimensions by a nonlinear system of partial differential equations in 3 dimensions, is applicable up to thousands of atoms (and hence the method of choice in most applications in materials science, molecular biology, and nanotechnology), but its modelling approximations have proven hard to systematically understand or improve despite great effort over many years.

Recent ideas to directly attack the curse of dimensionality of electronic wavefunctions which were presented at the workshop included: the derivation and implementation of symmetry-projected Hartree-Fock-Bogoliubov theory for molecular electronic structure problems (talk by Gustavo Scuseria); design of a stochastic 'game' of life, death and annihilation in Slater determinant space (talks by Ali Alavi and Alex Thom); the recently developed general mathematical format of truncation and low-rank approximation of tensors (talk by Wolfgang Hackbusch); quantum-chemical versions of the density matrix renormalization group algorithm

and its analysis in the context of the matrix product state alias TT tensor format (talk by Reinhold Schneider); the recent proof of high mixed regularity of Schrödinger electronic wavefunctions and its implications for efficient approximability in sparse bases (talk by Harry Yserentant); a sophisticated combination of coupled-cluster theory and low-rank approximation of tensors (talk by Alexander Auer); use of a Jastrow ansatz with prefactor optimization via a quantum Monte Carlo approach (talk by Heinz-Jürgen Flad), efficient iterative symmetry decomposition for large atoms (talk by Christian Mendl); hierarchical decomposition of total molecular energies into contributions from different bond orders (Frederik Heber); and use of a Smolyak grid and an efficient quadrature scheme built from nested 1D quadratures to solve the vibrational Schrödinger equation (talk by Tucker Carrington).

Another important aspect in computational cost reduction is the structure of the underlying single-particle basis sets. Werner Kutzelnigg presented sophisticated results on completeness and convergence rates for Gaussian and exponential bases, Lin Lin presented novel adaptive local basis sets for efficient density functional theory calculations in solids, and Peter Pulay gave a quantum chemist's view on basis sets based on his own more than 40 years of work in the area.

Volker Bach gave an overview over old and new mathematical results in Hartree-Fock theory, Thomas Oestergaard Soerensen explained his recent work on local analyticity of Schrödinger wavefunctions in the interparticle positions and distances, and Thorsten Rohwedder and Saber Trabelsi presented rigorous analyses of the coupled cluster equations respectively the multi-configuration time-dependent Hartree-Fock equations. Heinz Siedentop derived and analyzed a mathematical model for interacting Dirac Fermions in graphene quantum dots.

Progress related to multiscale aspects of many-electron systems included the derivation, analysis and implementation of a governing equation for the distortion in electronic structure caused by a defects in a solid (opening talk by Eric Cances). Note that in an approximating N-particle system the total energy is order N, but the desired energy contribution is order 1, and one needs to pass to the limit $N \to \infty$. Similar scale issues (with small parameter being the reciprocal of the number of particles) appear when one is interested in the energy required to perturb the density of a Fermi gas (talk by Mathieu Lewin) and the distortion of electronic structure in a solid by elastic deformation (talk by Jianfeng Lu). Another important small parameter appears in quantum molecular dynamics, namely the ratio between electronic and nuclear mass; this parameter is traditionally exploited both by adiabatic decoupling of electronic and nuclear motion (Born-Oppenheimer approximation) and semiclassical approximation of the nuclear motion. Subtle ways of exploiting this smallness even when the traditional assumptions of the Born-Oppenheimer approximation (namely uniform gaps between electronic energy levels) are violated were presented by Caroline Lasser (numerical approximations of quantum molecular dynamics) and Volker Betz (asymptotic analysis of quantum dynamics at avoided crossings of electronic

levels). George Hagedorn explained his recent derivation and analysis (and ensu-
ing predictions) of non-classical Born-Oppenheimer-type approximations for the
vibrational Schrödinger equation for hydrogen-bonded systems; here one exploits
the smallness of the mass of the hydrogen nucleus compared to the other nuclear
masses.

New examples of quasi-exactly soluble many-electron models were presented by
Jerzy Cioslowski (electrons in spherical confining potentials), Pierre-Francois Loos
(electrons restricted to hyperspheres), and Ben Goddard (highly charged atomic
ions).

Another highlight of the workshop was a very well attended Thursday evening
session with short presentations by the graduate students Virginie Ehrlacher,
Robert Lang, Stefan Kühn, André Uschmajew, Fabian Hantsch, and Stefan Hand-
schuh, which – just like the daytime lectures – were followed by lively discussion.

Workshop: Mathematical Methods in Quantum Chemistry

Table of Contents

Abstracts

Rate of convergence of basis expansions in Quantum Chemistry
WERNER KUTZELNIGG

1. BASIS EXPANSIONS. GENERAL

The simplest kind of a basis expansion is that of a *generalized Fourier expansion*. One expands a function $f(x)$ in an orthonormal basis $\{\chi_p^{(n)}\}$ that becomes complete (with an appropriate meaning) for $n \to \infty$

$$(1) \qquad f(x) = \lim_{n \to \infty} f_n(x); \ f_n(x) = \sum_{p=1}^{n} c_p^{(n)} \chi_p^{(n)}$$

This converges *exponentially*, in a Hilbert space norm, if $f(x)$ is differentiable an infinite number of times. Otherwise the convergence obeys an *inverse-power law* with a power depending on the differentiability of $f(x)$. Such a rate of convergence is unsatisfactory. There are two possibilities for an improvement:

(a) One augments the basis by one or more *comparison functions* [1] that describe the singularities of $f(x)$ correctly. Then the convergence still follows an inverse-power law, but with a higher exponent. This idea is used in the R_{12} method. In the traditional *configuration interaction* (CI) or *coupled-cluster* (CC) methods one expands the n-electron wave function in a basis of Slater determinants constructed from spin orbitals. In the R_{12} method [2] one includes contributions *linear* in the interelectronic distance r_{12} that cannot be expanded in this basis, but which are necessary to describe the correlation cusp [3] correctly. This improves the convergence in a spectacular way, with only a moderate increase of the computational effort. The results in a *given basis* are improved by *basis incomplete corrections*. Typical is a reduction of the error from $(L+1)^{-3}$ to $(L+1)^{-7}$ if L is the highest angular momentum quantum number of the basis functions. This idea is well established and is powerful. It will not be further pursued in the present lecture.

(b) One formulates the basis expansion as a discretized integral transformation, i.e. one starts from

$$(2) \qquad f(x) = \int_{-\infty}^{-\infty} g(x,y) dy$$

with $g(x,y)$ a *bell-shaped* function of y that decays as $\exp(-a|y|)$ with $a > 0$. For an appropriately chosen $g(x,y)$ one can truncate the integration domain on both sides which leads to a an *upper and a lower cut-off error* ε_{cu} and ε_{cl} respectively, and treat the remaining finite integration domain by the trapezoid approximation in terms of n intervals of the length h. One is on the safe side, if the sum $\varepsilon_c = \varepsilon_{cu} + \varepsilon_{cl}$ and the discretization error ε_d decay asymptotically as [4]

$$(3) \qquad \varepsilon_c \sim \exp(-ahn); \ \varepsilon_d \sim \exp(-b/h)$$

Then the best compromise is

$$(4) \qquad h \sim \frac{d}{\sqrt{n}}; \ \varepsilon \sim \exp(-k\sqrt{m})$$

This is *almost exponential* convergence. The error is [unlike that for an expansion of type (1)] insensitive to singularities of $f(x)$.

The different error contributions do not necessarily have the same sign (especially ε_d has an oscillatory dependence on h), and error cancellations are common, but do not raise serious problems.

Often one is not interested in a best *local* approximation of $f(x)$, but rather in the best approximation of a global property, e.g. a functional of $f(x)$. If $f(x)$ is a wave function, the *expectation value of the Hamiltonian* is a convenient global property. One can then achieve that all leading error contributions have the same sign.

2. Expansion of the H-atom ground state in a Gaussian basis

The error ε of the energy expectation value for the ground state of hydrogen-like ions

$$(5) \qquad \varepsilon = \int f(r)\{H - E_0\}f(r)r^2 dr; \ H = -\frac{1}{2}\Delta - \frac{Z}{r}; \ E_0 = -\frac{1}{2}Z^2$$

vanishes if $f(r)$ is the exact radial eigenfunction.

$$(6) \qquad f(r) = 2Z^{3/2}e^{-Zr} = \int_0^\infty \phi(s,r)ds; \ \phi(s,r) = \frac{Z^{5/2}}{\sqrt{\pi}}s^{-\frac{3}{2}}\exp(-\frac{Z^2}{4s} - sr^2)$$

This is a Gaussian integral transformation [5]. Integration over r leads to:

$$F(s,t) = \int_0^\infty dr \ r^2 \phi(s,r)(\hat{H} - E_0)\phi(t,r) =$$

$$\frac{\exp(-\frac{Z^2(s+t)}{4st})}{s^{\frac{3}{2}}t^{\frac{3}{2}}}\left\{ \frac{Z^7}{8\sqrt{\pi}}\frac{1}{(s+t)^{3/2}} - \frac{Z^6}{2\pi(s+t)} + \frac{3Z^5 st}{4\sqrt{\pi}(s+t)^{5/2}} \right\}$$

(7)

We introduce the mapping $s = e^p$; $t = e^q$, in the spirit of the *even-tempered* approximation, which transforms the integration domains from $[0,\infty]$ to $[-\infty,\infty]$ such that $\tilde{F}(p,q)$ is bell-shaped both as function of p and q. We get the cut-off errors [6]:

$$(8) \qquad \varepsilon_{cl} = \int_0^{s_l}ds\int_0^{s_l}dtF(s,t) = \frac{Z^3}{\sqrt{2}\pi}s_l^{-\frac{1}{2}}e^{-Z^2/2s_l}[1 + O(s_l)]$$

$$(9) \qquad \varepsilon_{cu} = -\int_{s_u}^\infty ds\int_{s_u}^\infty dtF(s,t) = \frac{Z^5}{6\sqrt{\pi}}(8 - 5\sqrt{2})s_u^{-\frac{3}{2}} + O(t_2^{-4})$$

For an even-tempered basis s_l and s_u are related as $s_u = s_l\exp(nh)$.

Minimization of $\varepsilon_c = \varepsilon_{c1} + \varepsilon_{c2}$ with respect to s_l, for fixed n and h, leads to the asymptotically leading terms:

$$(10) \qquad s_l = \frac{Z^2}{6hn}; \; \varepsilon_c = A(hn)^{\frac{3}{2}} e^{-\frac{3hn}{2}}$$

with A a numerical constant.

The leading term of the discretization error is [6]

$$(11) \qquad \varepsilon_d \sim \int_0^\infty ds \int_0^\infty dt F(s,t) \cos(\frac{2\pi \ln s}{h}) \cos(\frac{2\pi \ln t}{h}) \sim \frac{8\pi^4 Z^2}{h^3} e^{-2\pi^2/h}$$

Minimize the total error $\varepsilon = \varepsilon_c + \varepsilon_d$ with respect to h (for n fixed)

$$(12) \qquad h = \frac{2\pi}{\sqrt{3n}}; \; \varepsilon = Cn^{9/8} \exp\{-\pi\sqrt{3n}\}; \; s_l = \frac{Z^2}{2\pi\sqrt{3}} n^{-1/2}$$

The asymptotically (i.e. for large n) optimized parameters α and β of the even-tempered basis are [6]:

$$(13) \qquad \beta = m^{-1/(4m)} \exp(2\pi/\sqrt{3m}); \; \alpha = \frac{Z^2}{2\pi\sqrt{3m}} \exp\frac{\pi}{\sqrt{3m}}; \; \zeta_{m,k} = \alpha\beta^{(k-1)}$$

Error estimates are well represented by leading asymptotic terms.

Good agreement with purely numerical minimization.

Generalization to *arbitrary states* possible.

Different optimal parameters for different *properties* (e.g. distance in Hilbert space, variance of the energy, etc.)

Slight improvement if one *relaxes the even-tempered mapping.*

3. Expansion of a relativistic wave function in a kinetically balanced even-tempered basis

The normalized relativistic ground state wave function ψ of H-like ions has the large component φ and the small component χ

$$(14) \quad \varphi = R_g(r)\eta_{-1}^m; \; R_g(r) = N_g r^\nu e^{-Zr}; N_g = 2^{\nu+1} Z^{\nu+\frac{3}{2}} \sqrt{2+\nu}/\sqrt{\Gamma(3+2\nu)};$$
$$\nu = \sqrt{1 - Z^2/c^2} - 1 \approx -Z^2/(2c^2)$$

$$(15) \quad \chi = iR_f(r)\eta_1^m; \; R_f(r) = N_f r^\nu e^{-Zr}; N_f = -2^{\nu+1} Z^{\nu+\frac{3}{2}} \sqrt{-\nu}/\sqrt{\Gamma(3+2\nu)}$$

where η_κ^m is a normalized function of angular and spin variables for the quantum numbers κ and $m = m_j$. The radial factors have the the Gaussian integral transformation: [7]

$$(16) \quad R_g(r) = \int_0^\infty f_g(s,Z) \exp(-sr^2)ds; \; R_f(r) = \int_0^\infty f_f(s,Z)rs \exp(-sr^2)dr$$

$$(17) \quad f_g(s, Z) = Z^{\nu + \frac{5}{2}} 2^{\nu + 1} s^{-\frac{\nu}{2} - 1} \left[\Gamma(2\nu + 3\ ) \right]^{-\frac{1}{2}} \sqrt{2 + \nu}$$

$$\times \left\{ Z^{-1} \left[\Gamma \left(-\frac{\nu}{2} \right) \right]^{-1} M \left(1 + \frac{\nu}{2}, \frac{1}{2}, -\frac{Z^2}{4s} \right) \right.$$

$$\left. - s^{-\frac{1}{2}} \left[\Gamma \left(-\frac{\nu + 1}{2} \right) \right]^{-1} M \left(\frac{3 + \nu}{2}, \frac{3}{2}, -\frac{Z^2}{4s} \right) \right\}$$

$$(18) \quad f_f(Z, s) = Z^{\nu + \frac{3}{2}} 2^{\nu + 1} [\Gamma(2\nu + 3)]^{-\frac{1}{2}} s^{-\frac{\nu + 4}{2}} \sqrt{-\nu} \times$$

$$\left\{ Z \left[\Gamma \left(-\frac{\nu}{2} \right) \right]^{-1} M \left(1 + \frac{\nu}{2}, \frac{3}{2}, -\frac{Z^2}{4s} \right) \right.$$

$$\left. - \sqrt{s} \left[\Gamma \left(-\frac{\nu}{2} + \frac{1}{2} \right) \right]^{-1} M \left(\frac{1 + \nu}{2}, \frac{1}{2}, -\frac{Z^2}{4s} \right) \right\}$$

with $M(a, b, x)$, also known as $_1F_1(a, b, x)$, Kummer's confluent hypergeometric function.

This implies *kinetical balance*. If $\{\phi_k\}$ is a basis for the expansion of φ, the basis for χ is $\{\vec{\sigma} \cdot \vec{p} \phi_k\}$

More complicated than the non-relativistic counterpart, but manageable.

We should now consider the error of the energy expectation value

$$(19) \quad \langle \psi | D - E | \psi \rangle = \langle \varphi | V - E | \varphi \rangle + c \langle \varphi | \vec{\sigma} \cdot \vec{p} | \chi \rangle + c \langle \chi | \vec{\sigma} \cdot \vec{p} | \varphi \rangle + \langle \chi | V - E - 2mc^2 | \chi \rangle$$

which vanishes for φ and χ exact, but does not vanish for φ and χ approximate. Further details are similar to the non-relativistic case, just lengthier. The results are preliminary, since so far a simpler functional than (19) was considered.

The results for the upper and lower cut-off errors, as well as the discretization error are similar to the non-relativistic counterparts. The main difference is: nr: $\varepsilon_u \sim s_2^{-3/2}$; rel: $\varepsilon_u \sim s_2^{-1 - \nu/2}$

As a consequence to the leading order: nr: $\beta \sim \exp(2\pi/\sqrt{3n})$; rel: $\beta \sim \exp(2\pi/\sqrt{[2 + \nu]n})$

The exponents are steeper.

Final error estimate nr: $\varepsilon \sim \exp(-\pi\sqrt{3n})$; rel: $\varepsilon \sim \exp(-\pi\sqrt{[2 + \nu]n})$

The convergence is in the mean, but not pointwise. Divergence at the position of a point nucleus.

An even-tempered kinetically balanced basis is *complete* for the H-atom ground state [7]

4. EXPANSION OF THE FUNCTION $\frac{1}{r}$ IN A BASIS OF EXPONENTIAL FUNCTIONS

While the expansion of wave functions in Gaussian basis if of central importance in Quantum Chemistry, the related problem of the expansion of $\frac{1}{r}$ in a Gaussian or an exponential basis, is of less direct interest in atomic or molecular theory, this expansion is important for many physical problems. It is interesting to compare the application of the technique advocated here, with a recent study of the expansion in an exponential basis, where a completely different formalism was used [8]. This expansion is formally simpler than that of a wave function in a Gaussian basis.

This allows to study some aspects in more details. In particular we look now at the expansion in terms of local criteria.

We start from the inverse Laplace transform of $\frac{1}{r}$

$$(20) \qquad \frac{1}{r} = \int_0^\infty f(r,s)ds; \ f(r,s) = e^{-rs}$$

We arrive at an approximation of $\frac{1}{r}$ as a linear combination of exponentials via essentially the same steps as before:

1. We map the integration domain from $0 \le s \le \infty$ to $-\infty \le t \le \infty$ by means of the *even-tempered* mapping

$$(21) \qquad s(t) = e^t$$

such that the integrand $f(r,s)$ is replaced by

$$(22) \qquad g(r,t) = f(r,s[t])\frac{ds}{dt} = e^{-re^t}e^t; \ \int_{-\infty}^\infty g(r,t)dt = \frac{1}{r}$$

For $r > 0$, $g(r,t)$ is a bell-shaped, though rather asymmetric, function of t, that decays exponentially both for $t \to \infty$ and $t \to -\infty$.

2. We restrict the integration domain of (21) or (22) to $[s_l, s_u]$ or $[t_l, t_u]$ respectively. We obtain the lower (l) and upper (u) cut-off errors

$$(23) \qquad \varepsilon_{cl} = \int_0^{s_l} f(r,s)ds = \frac{1-e^{-rs_l}}{r} = s_l - \frac{s_l^2 r}{2} + O(r^2 s_l^3)$$

$$(24) \qquad \varepsilon_{cu} = \int_{s_u}^\infty f(r,s)ds = \frac{e^{-rs_u}}{r}$$

ε_{cl} is well represented by the leading term s_l if

$$r \ll 2/s_l$$

3. We introduce an equidistant grid with step length h in terms of the variable t, such that the grid points are *even tempered*

$$(25) \qquad t_k = t_l + kh; \ k = 0, ..., n; \ s_k = s_l \exp(kh)$$

This allows us to relate the cut-off parameters as

$$(26) \qquad t_u = t_l + hn; \ s_u = s_l e^{hn}$$

to the integration domain hn. We have $n+1$ grid points and n intervals of length h. We want to minimize the sum of two cut-off errors

$$(27) \qquad \varepsilon_c = \varepsilon_{cl} + \varepsilon_{cu} = s_u e^{-nh} + \frac{e^{-rs_u}}{r}$$

with respect to variation of s_u, which leads to

$$(28) \qquad 0 = \frac{d\varepsilon_c}{ds_u} = e^{-nh} - e^{rs_u}$$

$$(29) \qquad s_u = \frac{nh}{r}; \ s_l = \frac{nh}{r}e^{-nh}; \ \varepsilon_c = \frac{1+nh}{r}e^{-nh}$$

4. The leading term of the discretization error is obtained as

$$
(30) \qquad e_d = 2 \int_{t_l}^{t_u} g(r,t) \cos(\frac{2\pi t}{h}) dt = 2 \int_{s_l}^{s_u} f(r,s) \cos(\frac{2\pi \ln s}{h}) ds
$$

where $2\cos(\frac{2\pi t}{h})$ is the first term of the Fourier expansion of a periodic δ function with periodicity h.

We construct an optimum h as function of the number n of integration intervals by requiring that ε_c and ε_d have the same order of magnitude.

$$
(31) \qquad \varepsilon_{d\infty} = 2 \int_{-\infty}^{\infty} g(r,t) \cos(\frac{2\pi t}{h}) dt = 2 \int_{0}^{\infty} f(r,t) \cos(\frac{2\pi \ln s}{h}) ds
$$

$\varepsilon_c \geq 0$, i.e. the integral with cut-off always underestimates the full integral, but ε_d can be *positive or negative*, such that the two errors can either accumulate or cancel partially.

Further, while ε_c only depends on the length hn of the integration domain, ε_d depends strongly on the *position* of the grid with respect to the integrand, say relative to its maximum, or to the coordinate origin. Such a shift can be described by a phase θ in the integral, i.e. by considering

$$
\begin{aligned}
\varepsilon_{d\theta} &= 2 \int_{-\infty}^{\infty} g(r,t) \cos(\frac{2\pi t}{h} + \theta) dt = 2 \int_{0}^{\infty} f(r,t) \cos(\frac{2\pi \ln s}{h} + \theta) ds \\
(32) \qquad &= 2 \int_{0}^{\infty} \mathrm{Re}\{e^{-rs-i\theta} s^{-\frac{2\pi i}{h}}\} ds = 2\mathrm{Re}\{e^{-i\theta} r^{\frac{2\pi i}{h}-1} \Gamma(1 - \frac{2\pi i}{h})\}
\end{aligned}
$$

instead of $\varepsilon_{d\infty}$. A change of θ by 2π corresponds to a shift of the grid by one unit. As long as we have no unique prescription as to the placement of the grid, we can evaluate $e_{d\theta}$ for an unknown θ and construct an *average discretization error* e_{dav} as the mean square over θ.

$$
(33) \qquad \varepsilon_{dav} = \sqrt{\int_{0}^{2\pi} e_{d\theta}^2 d\theta/(2\pi)} = \frac{2\pi}{r} \frac{\sqrt{\mathrm{csch}(\frac{2\pi^2}{h})}}{h}
$$

If we realize that $\varepsilon_d = \mathrm{Re}\{D(h)\}$, where $D(h)$ is a complex function, we can use that

$$
(34) \qquad\qquad |\mathrm{Re}\{D(h)\}| \leq |D(h)|
$$

$D(h)$ (as well as its real and imaginary parts separately), is a rapidly oscillating function of h, but $|D(h)|$ depends smoothly on h.

While $D(h)$ depends strongly on a shift of the grid, as described by a phase θ, $|D(h)|$ is independent of θ. For $r \neq 1$ there is also an oscillating r-dependent factor $r^{\frac{2\pi i}{h}}$ in (32).

The asymptotic expansion of the upper bound for ε_{das} (which is not oscillating) for small h is

$$
(35) \qquad\qquad \varepsilon_{das} = \sqrt{2} e_{dav} = \frac{4\pi}{r\sqrt{h}} e^{-\frac{\pi^2}{h}} \{1 + O(\sqrt{h})\}
$$

6. The last step is now to determine h such that $\varepsilon_c = \varepsilon_{das}$

The exponential factors dominate both ε_c and ε_{das}. These factors are equal if

$$(36) \qquad h = \frac{\pi}{\sqrt{n}}$$

We make the ansatz

$$(37) \qquad h = \frac{\pi}{\sqrt{n}} + b\frac{\ln(n)}{n} + \frac{c}{n}$$

and determine b and c such that ε_c and ε_{dav} do not only agree in the exponential factors, but also in the leading prefactors.

Let us use the procedure to construct the pararameters that are optimal for, say, $r = 1$ and look at the error for $r \neq 1$. We have the parameters h as given by (37) as well as

$$(38) \qquad s_l(1) = \sqrt{2}\pi^{\frac{3}{4}}n^{\frac{3}{8}}e^{-\pi\sqrt{n}}; \; s_u(1) = s_l(1)e^{-hn} = \pi\sqrt{n} - \ln(\sqrt{2}\pi^{\frac{3}{4}}n^{\frac{3}{8}})$$

and the asymptotic r-dependent error contributions

$$\varepsilon_{cl}(r) \;\; = \;\; s_l(1); \; \varepsilon_{cu}(r) = \frac{e^{-rs_{u1}}}{r} = \frac{e^{-\pi r\sqrt{n}}}{r}(2^{\frac{1}{2}}n^{\frac{3}{8}}\pi^{\frac{3}{4}})^r$$

$$(39) \qquad \varepsilon_{das}(r) \;\; = \;\; 2\frac{\sqrt{2}}{r}\pi^{\frac{3}{4}}e^{-\pi\sqrt{n}}n^{\frac{3}{8}}$$

While $\varepsilon_{cl}(1) = \varepsilon_{cu}(1) = \frac{1}{2}\varepsilon_{das}(1)$, $\varepsilon_{cu}(r)$ dominates for $r \ll 1$ and is negligible for $r \gg 1$. In this regime, $\varepsilon_{cl}(r)$ approaches a constant value for large r, and is practically r-independent, while $\varepsilon_{cu}(r)$ decreases as $\sim \frac{1}{r}$.

The numerical error is, as it should, bounded by the asymptotic estimate. However, while our estimate depends smoothly on r, the numerical error oscillates strongly as function of r. This oscillation comes entirely from the discretization error. As we see from eqn. (32), $\varepsilon_{d\theta}$ contains an r-dependent oscillating factor

$$(40) \qquad \mathrm{Re}\{r^{\frac{2\pi i}{h}}\} = \mathrm{Re}\{\exp\frac{2\pi i\ln(r)}{h}\} = 2\cos\frac{2\pi\ln(r)}{h}$$

Although we have only cared for $r = 1$, we have obtained an approximation with a bounded estimate for the absolute error valid for $1 \leq r < \infty$.

We actually predict the estimate for the *absolute* error

$$(41) \qquad |\frac{1}{r} - p(r)| \leq \varepsilon_{as}(r) \leq \varepsilon_{as}(1) = 4\sqrt{2}\pi^{\frac{3}{4}}e^{-\pi\sqrt{n}}n^{\frac{3}{8}}$$

This estimate has its maximum for $r = 1$, and holds for all $r > 1$.

5. Minimization of the relative error

In the previous section we have, starting from a local approximation for $r = 1$, achieved a bound for the *absolute* error

$$(42) \qquad \varepsilon(r) = |\frac{1}{r} - p(r)|$$

valid for $r \geq 1$, of the approximation $p(r)$ as an exponential sum to $\frac{1}{r}$. We now care for the *relative* error

$$(43) \qquad \tilde{\varepsilon}(r) = r|\frac{1}{r} - p(r)| = |1 - rp(r)|$$

for $0 \leq r_1 \leq r \leq r_2$.

Again we decompose the error into three parts, of which we consider the asymptotically leading terms

$$(44) \qquad \tilde{\varepsilon}_{cl}(r) = rs_l; \ \tilde{\varepsilon}_{cu}(r) = e^{-rs_u}; \ \tilde{\varepsilon}_{das}(r) = \frac{4\pi}{\sqrt{h}}e^{-\frac{\pi^2}{h}}$$

If we choose s_l, s_u, h independent of r, we get

$$(45) \qquad 0 \leq \tilde{\varepsilon}_{cl}(r) \quad \leq \quad \tilde{\varepsilon}_{cl}(r_2) = r_2 s_l$$
$$(46) \qquad 0 \leq \tilde{\varepsilon}_{cu}(r) \quad \leq \quad \tilde{\varepsilon}_{cu}(r_1) = e^{-r_1 s_u}$$

We determine s_l and $s_u = s_l e^{hn}$ such that asymptotically $\tilde{\varepsilon}_{cl}(r_2) = \tilde{\varepsilon}_{cu}(r_1)$ and get so a bound for the sum of the two relative cut-off errors, valid for $0 \leq r_1 \leq r \leq r_2$. The result is

$$(47) \qquad s_l \quad = \quad \frac{e^{-hn}hn}{r_1}$$

$$(48) \qquad s_u \quad = \quad \{hn - \ln hn + \ln(\frac{r1}{r2})\}/r_1$$

$$(49) \qquad \tilde{\varepsilon}_c \quad = \quad \tilde{\varepsilon}_{cl} + \tilde{\varepsilon}_{cu} = 2e^{-hn}hn\frac{r_2}{r_1}$$

The relative cut-off error is proportional to $\frac{r_2}{r_1}$. We next determine h such the cut-off and the discretization errors agree to the leading order. We make the ansatz

$$(50) \qquad h = \frac{\pi}{\sqrt{n}} + \frac{a}{n} + \frac{b\ln n}{n} + \frac{c}{2n}\ln(\frac{r_2}{r_1})$$

and get finally

$$(51) \qquad h \quad = \quad \frac{\pi}{\sqrt{n}} + \frac{\ln(\pi/4)}{4n} + \frac{\ln n}{8n} + \frac{1}{2n}\ln(\frac{r_2}{r_1})$$

$$(52) \qquad \varepsilon \quad = \quad \varepsilon_c + \varepsilon_d = 4\sqrt{2}\pi^{\frac{3}{4}}n^{\frac{3}{8}}e^{-\pi\sqrt{n}}\sqrt{\frac{r_2}{r_1}}$$

The error bound now increases only as $\sqrt{\frac{r_2}{r_1}}$. This is a good approximation if

$$(53) \qquad \ln(\frac{r_2}{r_1}) \ll 2\pi\sqrt{n}$$

We get an asymptotic bound for the relative error as function of r in terms of

$$(54) \qquad \varepsilon_{as}(r) = s_l r + e^{-s_u r} + \varepsilon_{das}(r)$$

6. Alternative mappings

We start again from

$$(55) \qquad \frac{1}{r} = \int_0^\infty e^{-rs} ds$$

A different mapping [8]

$$(56) \qquad s(\tau) = \ln(e^\tau + 1); \ \tau = \ln(e^s - 1)$$

did not improve the rate of convergence. However, the following mapping looks promising.

$$(57) \qquad s = \exp(t - e^{-t})$$

such that our integrand becomes

$$(58) \qquad g(r,t) = \exp(-e^{-t} - e^{e^{-t} - t} r + t)(1 + e^{-t})$$

$$(59) \qquad \frac{1}{r} = \int_{-\infty}^\infty g(r,t) dt$$

Hopefully it improves the critical factor $\exp - \pi\sqrt{n}$ to $\exp - 2\pi\sqrt{n}$, as found numerically [8] without any constraint on the mapping function. It needs to be studied in more detail.

7. Use of global criteria

Rather than to care for an optimal approximation for some fixed r, one can use a global criterion for accuracy, somewhat as we have used it for the expansion of wave functions.

Let us regard $V(\vec{r}) = \frac{1}{r}$ as a prototype of a potential, namely that created by a point charge. We are mainly interested in expectation values or matrix elements of a potential in terms of wave functions, such as

$$(60) \qquad \langle \psi | V(\vec{r}) | \psi \rangle = \int |\psi(\vec{r})|^2 V(\vec{r}) d^3 r$$

with the normalized ground state wave function of a hydrogen-like ion with the nuclear charge α

$$(61) \qquad \psi(r) = 2\alpha^{\frac{3}{2}} \exp(-\alpha r); \int |\psi(r)|^2 r^2 dr = 1$$

and the potential created by the charge Z (which may differ from α). Both V and ψ are independent of the angular variables (θ, φ). In this case the expectation value involves the radial coordinate r only

$$(62) \qquad \langle \psi | \frac{Z}{r} | \psi \rangle = Z \int |\psi(r)|^2 r dr = Z\alpha$$

There are two complementary aspects. Here we take the exact ψ and expand $V(r)$ in a basis. Alternatively, as we have done in the first part of the lecture, we can take the exact $V(r)$ and expand ψ in a basis.

Let us insert the inverse Laplace transformation into the expectation value .

$$(63) \quad \langle\psi|\frac{Z}{r}|\psi\rangle = \int_0^\infty F(s)ds; \ F(s) = Z\int_0^\infty |\psi(r)|^2 f(r,s)r^2 dr = Z(1+\frac{s}{2\alpha})^{-3}$$

We treat now $F(s)$ for constant Z and α in the same way as we have treated $f(r,s)$ for constant r previously. We apply the even-tempered mapping and get

$$(64) \qquad\qquad G(t) = F(s[t])\frac{ds[t]}{dt} = \frac{8Z\alpha^3 e^t}{(2\alpha + e^t)^3}; \ \int_{-\infty}^\infty G(t) = Z\alpha$$

G(t) is a slightly asymmetric bell-shaped curve decaying exponentially for both $t \to \infty$ and $t \to -\infty$. For the lower and upper cut-off error we get

$$(65) \qquad\qquad e_{cl} = \int_0^{s_l} F(s)ds = Z\frac{\alpha s_l(4\alpha + s_l)}{(2\alpha + s_l)^2} = Zs_l + O(s_l^2)$$

$$e_{cu} = \int_{s_u}^\infty F(s)ds = Z\frac{4\alpha^3 s_u(2\alpha + s_u)}{(2\alpha + s_u)^2}$$

$$(66) \qquad\qquad = 4Z\alpha^3 s_u^{-2} + O(s_u^{-3})$$

In view of the even-tempered mapping we have

$$(67) \qquad\qquad\qquad s_u = s_l e^{hn}$$

We can achieve that the leading terms of e_{cl} and e_{cu} agree, if we choose

$$(68) \qquad\qquad s_l = 2^{\frac{2}{3}}\alpha\exp(-\frac{2hn}{3})$$

$$(69) \qquad\qquad s_u = 2^{\frac{2}{3}}\alpha\exp(\frac{hn}{3})$$

$$(70) \qquad\qquad e_{cl} = e_{cu} = Z\alpha 2^{\frac{2}{3}}\exp(-\frac{2hn}{3})$$

Next we evaluate the leading term of the discretization error.

$$e_{d\infty} = 2\int_0^\infty F(s)\cos(\frac{2\pi\ln s}{h})ds = \int_0^\infty \frac{8Z\alpha^3}{(2\alpha + s)^3}2\mathrm{Re}\{s^{2\pi i/h}\}$$

$$(71) \qquad = 4\alpha\pi^2 Z\left\{\frac{\mathrm{Re}([2\alpha]^{2\pi i/h})}{h} + 2\pi\frac{\mathrm{Im}([2\alpha]^{2\pi i/h})}{h^2}\right\}\mathrm{csch}(\frac{2\pi^2}{h})$$

While $\mathrm{csch}(\frac{2\pi^2}{h})$ is a smooth function of h, with the asymptotically leading term

$$(72) \qquad\qquad\qquad 2\exp(-\frac{2\pi^2}{h})$$

$\mathrm{Re}([2\alpha]^{2\pi i/h})$ and $\mathrm{Im}([2\alpha]^{2\pi i/h})$ are, for small h, rapidly varying functions of h. However, they are bounded

$$(73) \qquad\qquad |\mathrm{Re}([2\alpha]^{2\pi i/h})| \le 1; \ |\mathrm{Im}([2\alpha]^{2\pi i/h})| \le 1$$

If we consider further that the asymptotic behaviour of $e_{d\infty}$ is determined by the terms with $\frac{1}{h^2}$, we get the following asymptotic estimate

$$(74) \qquad |e_{d\infty}| \le e_{das} = 8\alpha Z \pi^3 h^{-2} \exp(-\frac{2\pi^2}{h})$$

The overall error is determined by the factor $\exp(-2\pi\sqrt{\frac{n}{3}})$.

The expansion of $\frac{1}{r}$ in a Gaussian basis follows similar patterns, but the algebra is more complicated.

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Electrons in Spherical Confining Potentials

Jerzy Cioslowski

The talk concerns two recent developments in the field of Coulombic systems subject to spherical confinements, namely:

1. Shell Model Of Assemblies Of Equicharged Particles Subject To Radial Confining Potentials

A shell model of an assembly of N equicharged particles subject to an arbitrary radial confining potential $N\,W(r)$, where $W(r)$ is parameterized in terms of an auxiliary function $\Lambda(t)$, is presented. The validity of the model requires that $\Lambda(t)$ is strictly increasing and concave for any $t \in (0,1)$, $\Lambda'(0)$ is infinite, and $\tilde{\Lambda}(t) = -t^{-1} \Lambda'(t)/\Lambda''(t)$ is finite at $t = 0$. At the bulk limit of $N \to \infty$, the model is found to correctly reproduce the energy per particle pair and the mean crystal radius $R(N)$, which are given by simple functionals of $\Lambda(t)$ and $\Lambda'(t)$, respectively. Explicit expressions for an upper bound to the cohesive energy and the large-N asymptotics of $R(N)$ are obtained for the first time. In addition, variational formulation of the cohesive energy functional leads to a closed-form asymptotic expression for the shell occupancies. All these formulae involve the constant ξ that enters the expression $-(\xi/2)\,n^{3/2}$ for the leading angular-correlation correction to the minimum energy of n electrons on the surface of a sphere with a unit radius (the solution of the Thomson problem). The approximate energies, which constitute rigorous upper bounds to their exact counterparts for any value of N, include

the cohesive term that is not accounted for by the mean-field (fluid-like) theory and its simple extensions but completely neglect the surface-energy correction proportional to N.

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2. The Weak-correlation Limit Of Three-dimensional Quantum Dots With Three Electrons

Asymptotic energy expressions for the weak-correlation limits of the two lowest-energy states of three-dimensional quantum dots with three electrons are obtained in closed forms. When combined with the known results for the strong-correlation limit, those expressions, which are correct throughout the second order of perturbation theory, yield robust Padé approximants that allow accurate estimation of energies in question for all magnitudes of the confinement strength.

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Local defects in quantum crystals

Eric Cancès

(joint work with A. Deleurence, V. Ehrlacher, M. Lewin)

The modelling and simulation of the electronic structure of crystals is a prominent topic in solid-state physics, materials science and nano-electronics. Besides its importance for the applications, it is an interesting context for mathematicians for it gives rise to many interesting mathematical and numerical questions. The mathematical difficulties originate from the fact that crystals consist of infinitely many charged particles (positively charged nuclei and negatively charged electrons) interacting with Coulomb potential. Of course, a real crystal contains a finite number of particles, but in order to understand and compute the macroscopic properties of a crystal from first principles, it is in fact easier, or at least not more complicated, to consider that we are dealing with an infinite system.

The first mathematical studies of the electronic structure of crystals were concerned with the so-called thermodynamic limit problem for perfect crystals. As opposed to real crystals, which contain local defects (vacancies, interstitial atoms, impurities) and extended defects (dislocations, grain boundaries), perfect crystals are periodic arrangements of nuclei and electrons, in the sense that both the nuclear density and the electronic density are $\mathcal{R}$-periodic distributions, $\mathcal{R}$ denoting some discrete periodic lattice of $\mathbb{R}^3$. The thermodynamic limit problem for perfect crystals can be stated as follows. Starting from a given electronic structure model for finite molecular systems, find an electronic structure model for perfect crystals, such that when a cluster grows and "converges" (in some sense, see [5]) to some $\mathcal{R}$-periodic perfect crystal, the ground state electronic density of the cluster converges to the $\mathcal{R}$-periodic ground state electronic density of the perfect crystal.

For Thomas-Fermi like models, it is not difficult to guess what should be the corresponding models for perfect crystals. On the other hand, solving the thermodynamic limit problem, that is proving the convergence property discussed above, is much more difficult. This program was carried out for the Thomas-Fermi (TF) model in [12] and for the Thomas-Fermi-von Weizsäcker (TFW) model in [5]. Note that these two models are strictly convex in the density, and that the uniqueness of the ground state density is an essential ingredient of the proof.

The case of Hartree-Fock and Kohn-Sham like models is more involved. In these models, the electronic state is described in terms of electronic density matrices. For a finite system, the ground state density matrix is a non-negative trace-class self-adjoint operator, with trace N, the number of electrons in the system. For infinite systems, the ground state density matrix is no longer trace-class, which significantly complicates the mathematical arguments. Yet, perfect crystals being periodic, it is possible to make use of Bloch-Floquet theory and guess the structure of the periodic Hartree-Fock and Kohn-Sham models. These models are widely used in solid-state physics and materials science. The thermodynamic limit problem seems out of reach with state-of-the-art mathematical tools, except in the special case of the restricted Hartree-Fock (rHF) model, also called the Hartree

model in the physics literature. Thoroughly using the strict convexity of the rHF energy functional with respect to the electronic density, Catto, Le Bris and Lions were able to solve the thermodynamic limit problem for the rHF model [6].

Very little is known about the modelling of perfect crystals within the framework of the N-body Schrödinger model. To the best of our knowledge, the only available results [7, 10] state that the energy per unit volume is well defined in the thermodynamic limit. So far, the Schrödinger model for periodic crystals is still an unknown mathematical object.

The mathematical analysis of the electronic structure of crystals with defects has been initiated in [2] for the rHF model. This work is based on a simple idea whose rigorous implementation however requires some effort. This idea is very similar to that used in [8, 9] to properly define a no-photon QED model for atoms and molecules. Loosely speaking, it consists in considering the defect (the atom or the molecule in QED) as a quasiparticle embedded in a well-characterized background (a perfect crystal in our case, the polarized vacuum in QED), and to build a variational model allowing to compute the ground state of the quasiparticle.

In [2], such a variational model is obtained by passing to the thermodynamic limit in the difference between the ground state density matrices obtained respectively with and without the defect (and with periodic boundary conditions). The rHF ground state density matrix of an insulating or semiconducting crystal in the presence of a local defect can be written as $\gamma = \gamma_{\mathrm{per}}^0 + Q$, where γ_{per}^0 is the density matrix of the host perfect crystal (an orthogonal projector on $L^2(\mathbb{R}^3)$ with infinite rank which commutes with the translations of the lattice) and Q a self-adjoint Hilbert-Schmidt operator on $L^2(\mathbb{R}^3)$. Although Q is not trace-class in general [4], it is possible to give a sense to its generalized trace $\mathrm{Tr}_0(Q) := \mathrm{Tr}(Q^{++}) + \mathrm{Tr}(Q^{--})$, where

$$Q^{++} := (1 - \gamma_{\mathrm{per}}^0)Q(1 - \gamma_{\mathrm{per}}^0) \text{ and } Q^{--} := \gamma_{\mathrm{per}}^0 Q \gamma_{\mathrm{per}}^0$$

(as γ_{per}^0 is an orthogonal projector, $\mathrm{Tr} = \mathrm{Tr}_0$ on the space of the trace-class operators on $L^2(\mathbb{R}^3)$), as well as to its density ρ_Q. The latter is defined by

$$\forall W \in C_{\mathrm{c}}^\infty(\mathbb{R}^3), \quad \mathrm{Tr}_0(QW) = \int_{\mathbb{R}^3} \rho_Q W.$$

The function ρ_Q is not in $L^1(\mathbb{R}^3)$ in general, but only in $L^2(\mathbb{R}^3) \cap \mathcal{C}$, where $\mathcal{C}$ is the Coulomb space, that is the space of charge distributions with finite Coulomb energy. An important consequence of these results is that

- in general, the electronic charge of the defect can be defined neither as $\mathrm{Tr}(Q)$ nor as $\int_{\mathbb{R}^3} \rho$;
- it may happen that $\rho_Q \in L^1(\mathbb{R}^3)$ but $\mathrm{Tr}_0(Q) \neq \int_{\mathbb{R}^3} \rho_Q$ (while we would have $\rho_Q \in L^1(\mathbb{R}^3)$ and $\mathrm{Tr}_0(Q) = \mathrm{Tr}(Q) = \int_{\mathbb{R}^3} \rho_Q$ if Q were a trace-class operator). In this case, $\mathrm{Tr}_0(Q)$ and $\int_{\mathbb{R}^3} \rho_Q$ can be interpreted respectively as the *bare* and *renormalized* electronic charges of the defect [4].

For a given nuclear charge of the defect, the bare (resp. the renormalized) electronic charge of the defect can *a priori* take several values [3], depending on the

choice of the Fermi level (i.e. of the chemical potential of the electrons). Yet, if the Coulomb energy of the nuclear charge ν of the defect is small enough and if m is integrable, the bare and renormalized electronic charges of the defect are independent of the choice of the Fermi level, and are respectively equal to 0 and $\frac{L_0}{1+L_0} \int_{\mathbb{R}^3} \nu$, where $0 < L_0 < \infty$ is a constant depending only on the host crystal [4]. Consequenly the renormalized total charge is given by

$$\int_{\mathbb{R}^3} \nu - \frac{L_0}{1 + L_0} \int_{\mathbb{R}^3} \nu = \frac{\int_{\mathbb{R}^3} \nu}{(1 + L_0)}.$$

The charge ν is thus partially screened by a factor $1 < (1+L_0) < \infty$. Full screening would correspond to $L_0 = +\infty$ and to a renormalized total charge equal to zero.

Let us emphasize that the results in [2, 4] are limited to insulators and semiconductors, characterized in the rHF setting by the fact that there is a positive gap between the Zth and $(Z+1)^{\text{st}}$ bands of the spectrum of the mean-field Hamiltonian of the perfect crystal, where Z is the number of electrons per unit cell. The mathematical arguments in [2, 4] cannot be straightforwardly adapted to the "metallic" case (absence of gap). In [12], Lieb and Simon have proved full screening for the TF model, under the assumption that the host crystal is a homogeneous medium. In [1], we focus on the TFW model [11] and prove that, in this framework, defects are always neutral (the charge ν is fully screened). As a consequence, the TFW model cannot be used to model insulating or semiconducting crystals, for which the screening effect is only partial, and in which charged defects can be observed.

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How Much Energy Does it Cost to Make a Hole in the Fermi Sea?

Mathieu Lewin

(joint work with Rupert L. Frank, Elliott H. Lieb and Robert Seiringer)

Before addressing the question in the title, let us go back in time and discuss a simpler problem, which has been solved by Lieb and Thirring [8, 9] in 1975. Given a density $\rho(\mathbf{r})$ (a positive integrable function on $\mathbb{R}^3$), what is the kinetic energy cost to create a pile of $N = \int_{\mathbb{R}^3} \rho(\mathbf{r}) \, dr$ electrons having the given density $\rho(\mathbf{r})$? Because an electron can be given large momentum without changing its density, this energy can be arbitrarily large and a better question is to ask for the *minimal* kinetic energy cost.

Let us formalize this mathematically. The kinetic energy of any (mixed) quantum state can be expressed as $\mathrm{tr}(-\Delta\gamma)$, where γ is the corresponding one-particle density matrix [7], $\Delta = \nabla^2$ being the Laplacian (in units such that $m = 1/2$ and $\hbar = 1$). The self-adjoint operator γ acts on $L^2(\mathbb{R}^3, \mathbb{C}^q)$ where q is the number of internal degrees of freedom ($q = 2$ for electrons) and it must satisfy the following constraint $0 \le \gamma \le 1$ in the sense of self-adjoint operators. The kernel $\gamma(\mathbf{r}, \mathbf{r}')_{\sigma,\sigma'}$ of γ is a $q \times q$ matrix for every $(\mathbf{r}, \mathbf{r}') \in \mathbb{R}^6$ and the corresponding density is defined as $\rho_\gamma(\mathbf{r}) = \sum_{\sigma=1}^q \gamma(\mathbf{r}, \mathbf{r})_{\sigma,\sigma}$.

Coleman has shown in [1] that there is no further necessary condition on γ, that is, any operator $0 \le \gamma \le 1$ with $\mathrm{tr}\,\gamma = \int_{\mathbb{R}^3} \rho_\gamma = N$ arises from at least one (mixed) N-body quantum state. This allows us to define the minimal energy cost as

$$(1) \qquad\qquad \mathcal{T}(\rho) = \inf_{\substack{0 \le \gamma \le 1 \\ \rho_\gamma = \rho}} \mathrm{tr}(-\Delta\gamma).$$

In a semi-classical approximation, we think of putting the electrons in small boxes in phase space, of volume $(2\pi)^3$. The semi-classical approximation to $\mathcal{T}(\rho)$ is then [12, 3]

$$\mathcal{T}_{\mathrm{sc}}(\rho) = (2\pi)^{-3} q \int_{\mathbb{R}^3} dr \int_{p \le \left(\frac{6\pi^2 \rho(\mathbf{r})}{q} \right)^{1/3}} p^2 \, dp = K_{\mathrm{sc}}(3) \int_{\mathbb{R}^3} \rho(\mathbf{r})^{\frac{5}{3}} \, dr,$$

where $K_{\mathrm{sc}}(3) = (3/5)(6\pi^2/q)^{2/3}$. Lieb and Thirring have shown in [8, 9] that, up to a universal constant, semi-classics provides a universal lower bound to the true minimal quantum energy cost, even far from the semi-classical regime. The statement in any dimension is

$$(2) \qquad\qquad \mathcal{T}(\rho) \ge \tilde{K}(d) \int_{\mathbb{R}^d} \rho(\mathbf{r})^{1+\frac{d}{2}} \, dr$$

where $\tilde{K}(d)$ is a universal constant depending only on the space dimension d, and such that

$$\tilde{K}(d) \le K_{\mathrm{sc}}(d) := \frac{d}{d+2} \left(\frac{d(2\pi)^d}{q \, |S^{d-1}|} \right)^{\frac{2}{d}}.$$

It is widely believed that $\tilde{K}(d) = K_{\mathrm{sc}}(d)$ for $d \geq 3$. The best estimate known so far in dimension 3 is $\tilde{K}(3) \geq 0.6724\, K_{\mathrm{sc}}(3)$, see [2]. Since its invention, the Lieb-Thirring inequality has played an important role for the study of large quantum systems and of their stability [6, 7].

The dual version of the Lieb-Thirring inequality (2) is sometimes useful. Let $V(\mathbf{r})$ be a real-valued potential (the variable dual to $\rho(\mathbf{r})$). The sum of the negative eigenvalues of $-\Delta + V(\mathbf{r})$ can be expressed by a variational principle, leading to the estimate

$$\sum_{\lambda_i \leq 0} \lambda_i(-\Delta + V) = \inf_{0 \leq \gamma \leq 1} \operatorname{tr}\big((-\Delta + V)\gamma\big)$$

$$\geq \inf_{\rho \geq 0} \int_{\mathbb{R}^d} \Big(\tilde{K}(d)\rho(\mathbf{r})^{1+2/d} + V(\mathbf{r})\rho(\mathbf{r})\Big)\, dr$$

$$(3) \qquad\qquad = -\tilde{L}(d) \int_{\mathbb{R}^d} V(\mathbf{r})_-^{1+d/2}\, dr,$$

where $x_- = -\min(0, x)$ is the negative part of a number x and

$$\tilde{L}(d) = \frac{2}{d+2}\left(\frac{d}{(d+2)\,\tilde{K}(d)}\right)^{d/2}.$$

It can actually be shown that the inequality (3) is equivalent to (2).

A question that is not only natural but of significance for condensed matter physics is the analogue of (2) when we start, not with the vacuum, but with a background of fermions with some prescribed density $\rho_0 > 0$. In [4], we have estimated the minimal energy cost to go from an infinitely extended free Fermi gas of constant density $\rho_0 > 0$ to a density $\rho(\mathbf{r}) = \rho_0 + \delta\rho(\mathbf{r})$. Note that $\delta\rho(\mathbf{r})$ has no sign *a priori*. It can be negative (hence the word 'hole' in our title) as soon as $\delta\rho(\mathbf{r}) \geq -\rho_0$. The main difficulty is that we are perturbing an infinite quantum system, spread over the whole space. Nevertheless, we have been able to prove that semi-classics again gives a lower bound to the energy cost.

To formulate our result properly, let us recall that the Fermi level μ is linked to the density ρ_0 by the formula

$$\rho_0 = \frac{q}{(2\pi)^d} \int_{k^2 \leq \mu} dk = \frac{q\,|S^{d-1}|}{d\,(2\pi)^d}\, \mu^{\frac{d}{2}}$$

in any dimension $d \geq 1$. The one-particle density matrix of the free Fermi sea is the spectral projector $\Pi^- := \chi_{(-\infty,\mu)}(-\Delta)$ corresponding to filling all the energies $\leq \mu$. Our inequality can now be stated as follows, in space dimensions $d \geq 2$:

$$(4) \quad \operatorname{tr}\left(-\Delta - \mu\right)\left(\gamma - \Pi^-\right)$$

$$\geq K(d) \int_{\mathbb{R}^d} \left(\rho_\gamma(\mathbf{r})^{1+\frac{2}{d}} - (\rho_0)^{1+\frac{2}{d}} - \frac{2+d}{d}\,(\rho_0)^{\frac{2}{d}}\left(\rho_\gamma(\mathbf{r}) - \rho_0\right)\right) dr$$

for any one-particle density matrix $0 \leq \gamma \leq 1$. The term on the left side is non-negative, which follows from the fact that Π^- minimizes the free energy with chemical potential μ. The integrand on the right side is also non-negative, which

follows this time from the convexity of $\rho \mapsto \rho^{1+2/d}$. It behaves like $(\rho(\mathbf{r}) - \rho_0)^2$ for $\rho(\mathbf{r}) \simeq \rho_0$ and like $\rho(\mathbf{r})^{1+2/d}$ for large $\rho(\mathbf{r})$, as in the usual Lieb-Thirring inequality (2). Taking $\rho_0 \to 0$ we actually recover (2) in the limit. The optimal constant $K(d)$ is independent of $\rho_0 > 0$ (by scaling) but it does not necessarily coincide with the optimal constant $\tilde{K}(d)$ of (2) for $\rho_0 = 0$. The inequality (4) is *not* valid in dimension $d = 1$, as we will explain later.

As for the usual Lieb-Thirring case, there is a dual inequality. Let us consider a real-valued potential $V(\mathbf{r}) \in L^2(\mathbb{R}^d) \cap L^{1+d/2}(\mathbb{R}^d)$, for $d \geq 2$. Then we have

(5) $\quad \mathrm{tr}(-\Delta - \mu + V)(\Pi_V^- - \Pi^-)$

$$\geq -L(d) \int_{\mathbb{R}^d} \left((V(\mathbf{r}) - \mu)_-^{1 + \frac{d}{2}} - \mu^{1 + \frac{d}{2}} + \frac{2+d}{2} \mu^{\frac{d}{2}} V(\mathbf{r}) \right) dr,$$

where $\Pi_V^- := \chi_{(-\infty,\mu)}(-\Delta + V)$ is the one-particle density matrix of the perturbed Fermi sea in presence of the potential V. The integrand on the right side behaves like $V(\mathbf{r})^2$ for small $V(\mathbf{r})$ and $V(\mathbf{r})_-^{1+d/2}$ for large $V(\mathbf{r})$. The left side is *formally* equal to

$$\mathrm{tr}(-\Delta - \mu + V)(\Pi_V^- - \Pi^-) \text{ “ = ” } - \mathrm{tr}(-\Delta + V - \mu)_- + \mathrm{tr}(-\Delta - \mu)_- - \rho_0 \int_{\mathbb{R}^3} V(\mathbf{r})\, dr$$

but the first two terms on the right are infinite and the third is only finite under the additional assumption that $V \in L^1(\mathbb{R}^d)$. Note that the term $\rho_0 \int_{\mathbb{R}^3} V(\mathbf{r})\, dr$ is obtained by first order perturbation theory.

Second order perturbation theory predicts that

(6) $\quad \displaystyle\lim_{\epsilon \to 0} \frac{\mathrm{tr}(-\Delta - \mu + \epsilon V)(\Pi_{\epsilon V}^- - \Pi^-)}{\epsilon^2} = -\mu^{\frac{d}{2}-1} \int_{\mathbb{R}^d} \Psi_d \left(\frac{k}{\sqrt{\mu}} \right) |\widehat{V}(\mathbf{k})|^2\, dk$

where Ψ_d is the linear response function of the Fermi sea, which can be computed explicitly. In dimension $d = 1$,

$$\Psi_1(|k|) = \frac{1}{4\pi |k|} \log \left(\frac{2 + |k|}{|2 - |k||} \right)$$

is divergent at $k = \pm 2$, which is related to the so-called Peierls instability [10]. On the contrary, the semi-classical function satisfies

$$\lim_{\epsilon \to 0} \int_{\mathbb{R}^d} dr\, \frac{(\epsilon V(\mathbf{r}) - \mu)_-^{1+\frac{d}{2}} - \mu^{1+\frac{d}{2}} + \frac{2+d}{2} \mu^{\frac{d}{2}} \epsilon V(\mathbf{r})}{\epsilon^2} = -\frac{d(d+2)}{8} \mu^{\frac{d}{2}-1} \int_{\mathbb{R}^d} V(\mathbf{r})^2 dr$$

in any dimension $d \geq 1$. This proves that there *cannot* be a Lieb-Thirring inequality of the form of (5) in dimension $d = 1$. In higher dimensions $d \geq 2$, Ψ_d is a bounded function and there is no problem.

In the original works [8, 9], the potential Lieb-Thirring estimate (3) was derived first by spectral methods and the density estimate (2) was then obtained by using the equivalence. Until recently, there was no known direct proof of the density estimate (2). The situation changed last year when Rumin [11] found a simple

method to directly prove (2). Our method to tackle the positive density estimate show (4) is partly based on Rumin's ideas.

Our estimates (4) and (5) can be generalized in several directions. They are valid at positive temperature, and also when the ideal Fermi gas is replaced by a periodic background, under generic assumptions on the Fermi surface [5].

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Towards the optimal basis set in Kohn-Sham density functional theory

LIN LIN

(joint work with Weinan E, Jianfeng Lu and Lexing Ying)

Kohn-Sham density functional theory (KSDFT) is by far the most widely used electronic structure theory for condensed matter systems. However, the computational cost of the standard method for solving KSDFT increases cubically with respect to the number of electrons in the system (N). The cubic scaling hinders the application of KSDFT to systems of large size.

Our aim is to design accurate and efficient algorithms to solve KSDFT for both insulating and metallic systems [1, 2, 3, 4, 5, 6, 7]. The electron density ρ depends only on the diagonal of the Fermi-Dirac operator (β: inverse temperature; μ:

chemical potential)

$$(1) \qquad\qquad \rho = \text{diag } f(H) \equiv \text{diag } \frac{2}{1 + e^{\beta(H-\mu)}}.$$

Our method directly targets at the calculation of the diagonal elements of the Fermi-Dirac operator, and thus reduces the computational cost for solving KSDFT. Specifically, the computational cost of our method is $\mathcal{O}(N)$ for one dimensional systems, $\mathcal{O}(N^{1.5})$ for two-dimensional systems, and $\mathcal{O}(N^2)$ for three-dimensional systems.

In this talk I focus on the reduction of the discretization cost for solving KS-DFT. The discretization cost is characterized by the number of basis functions per atom to discretize the Kohn-Sham Hamiltonian operator, and is a crucial factor in the total computational cost. Take the planewave discretization for instance, the number of basis functions is generally $500 \sim 5000$ even in the pseudopotential framework. The discretization cost can be significantly reduced to $20 \sim 80$ basis functions per atom by means of e.g. atomic orbital type basis functions, but these basis functions are based on explicit knowledge of the underlying system, and are often difficult to be systematically improved in practice. To overcome the problem of both the planewave basis functions and the atomic orbital type basis functions, we propose a novel discretization scheme called the adaptive local basis functions [4]. The adaptive local basis functions do not require explicit knowledge of the system, and are systematically obtained by solving a series of KSDFT problems of small size. The adaptive local basis functions achieve high accuracy (below 10^{-3} Hartree/atom) in the total energy calculation with the number of basis functions per atom close to the minimum possible number, namely the number of basis functions used by the tight binding method. The adaptive local basis functions are localized in the real space, and are discontinuous in the global domain. The continuous Kohn-Sham orbitals and the electron density are evaluated from these discontinuous basis functions using the discontinuous Galerkin (DG) framework. We demonstrate that primitive implementation of the adaptive local basis functions is already able to calculate the total energy for systems consisting of thousands of atoms.

The adaptive local basis functions are accurate, efficient, simple and systematically improvable in the total energy calculation. One potential drawback of the adaptive local basis functions is that the accuracy of the force calculation may not be systematically controlled. It is well known that if the basis functions change with respect to the atomic positions, the Hellmann-Feynman force is not accurate enough, and the Pulay force should be added [8]. The calculation of the Pulay force can be expensive since the derivatives of the basis functions with respect to all the atomic positions are to be computed. To overcome this drawback, we develop the optimized local basis functions [5] that inherit all the advantages of the adaptive local basis functions, and can systematically improve the accuracy of the force calculation. The optimized local basis functions are obtained by solving a variational problem in a prescribed primitive basis set that is independent of the atomic positions. When the optimality condition is satisfied, the contribution

of the Pulay force vanishes and the total force is equal to the Hellmann-Feynman force. This makes the optimized local basis functions an ideal tool for *ab initio* molecular dynamics as well as geometry optimization. We develop a preconditioned GMRES algorithm to obtain the optimized local basis functions in practice. Numerical results using a one dimensional model problem indicate that the optimized local basis functions can accurately compute the energy and the force along the trajectory of the molecular dynamics without systematic drift, using a very small number of basis functions per atom.

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A Modified Born–Oppenheimer Approximation for Hydrogen Bonding

George A. Hagedorn

(joint work with Alain Joye)

The standard time–independent Born–Oppenheimer approximation often yields substantially inaccurate vibrational energy levels for molecules that contain hydrogen bonds. In particular, the vibrational energy levels associated with oscillations of the hydrogen nucleus involved in the hydrogen bonding are often far from accurate. In this talk, we summarize the results of a joint project with Alain Joye to produce a better approximation that is still amenable to practical computation.

The detailed results of the project are presented in two papers, [5, 7]. Two other summaries (and a generalization) are presented in conference proceedings articles, [6, 8].

The reason the results were published in two separate papers is that we considered two different situations. In the first paper, [5], we studied the symmetric hydrogen bonds. In this case, we considered a molecule that consisted of two identical components that were bound together by a hydrogen bond. The molecule

thus had a reflection symmetry. As an example, we presented detailed results for the FHF^- ion. In the second paper, [7], we studied the situation where there was no such symmetry. The concrete example we presented was the $FHCl^-$ ion.

As we were completing this work, we learned of a related paper, [10], that empirically related vibrational energies of protons involved in hydrogen bonds with how symmetrical the hydrogen bond was. That paper considered some non-symmetric molecules that were very close to being symmetrical. In practice, our results are not likely to yield much useful information in these "almost symmetrical" situations since they are near the borderline between our two different modified approximations.

Standard Born–Oppenheimer approximations rely on the smallness of the parameter ϵ, where the nuclear masses are taken proportional to ϵ^{-4} and the electron masses are held fixed. The original work in this subject is [1], and there is now a substantial mathematical literature on this subject. See, $e.g.$, [2, 3, 4, 9]. Molecular energy levels have asymptotic expansions to all orders in even powers of ϵ. The ϵ^0 term arises from the energy of the electrons with the nuclei at optimal configurations. The ϵ^2 term consists of the harmonic approximations to the vibrations of the nuclei about the optimal configurations. The ϵ^4 term contains an electron energy correction, the lowest order anharmonic corrections to the vibrational energies, an uninteresting term related to removal of the center of mass motion, and the leading order rotational energy of the molecule.

For symmetric hydrogen bonds, we make two modifications. First, we take the mass of the hydrogen nucleus to be proportional to ϵ^{-3}. This is motivated by the observation that if the nucleus of (the most common isotope of) carbon is ϵ^{-4}, then the mass of a hydrogen nucleus is $1.015\,\epsilon^{-3}$. Second, the electron energy level is the effective potential felt by the nuclei, and we modify one coefficient in its Taylor series approximation around the optimal nuclear configuration. If Z denotes the coordinate for the hydrogen nucleus between the other two components of the molecule, we replace the quadratic term in the Taylor approximation, $a\,Z^2$, by $(a/\epsilon)\,\epsilon\,Z^2$. We numerically divide in the factor (a/ϵ) with the true value of $\epsilon = 0.0821$, but algebraically multiply by the small parameter ϵ. This is motivated by looking at examples and observing that the typical value of a is small in real molecules, and that $(a/0.0821)$ is typically roughly of order 1.

Thus, in our model, the small parameter ϵ plays two roles. It is involved in the scaling of the masses, and it also appears in the expression we use for the electronic potentially energy surface.

In the symmetric situation, we prove that with this modified model, the molecular energy has a full asymptotic expansion in powers of $\epsilon^{1/2}$. Our main interest is in the vibrational energies, which appear to leading order at order ϵ^2, as in the standard approximation. However, they are not described by a harmonic oscillator. To leading order, they are described by the energy levels of a quantum Hamiltonian that contains certain cubic and quartic terms as well as quadratic terms.

For the FHF^- ion, the standard harmonic approximation predicts the energy of the "asymmetric stretch," in which the hydrogen nucleus oscillates between its heavier neighbors, to be 1118 cm^{-1}, whereas an experimental value is 1331 cm^{-1}. Our model produces a much more accurate 1399 cm^{-1}.

For non-symmetric hydrogen bonds, we again modeled the hydrogen mass by $1.015\,\epsilon^{-3}$, but this time we made a different modification to the electronic potential energy surface. In the Taylor expansion, we made no changes to the terms that involved the hydrogen nucleus and its closest neighboring nucleus. For all terms that involve the heavy nucleus of the hydrogen bond that is farther from the hydrogen nucleus, we numerically divide the coefficient by $\epsilon = 0.0821$ and multiply algebraically by the small parameter ϵ. This is motivated from examining the electronic potential energy surface for the $FHCl^-$ ion. From numerical calculations, this ion behaves like FH with an internuclear distance of roughly 1 Angstrom, and a Cl^- ion roughly 2 Angstroms for the H nucleus. Since the H–Cl^- distance is large, all interactions involving the Cl^- are small.

In the non-symmetric situation, our model yields an asymptotic expansion in powers of $\epsilon^{1/4}$, but the vibrations associated with the hydrogen bond appear at different orders. The oscillations of the bond between the hydrogen nucleus and its nearest neighbor are of order $\epsilon^{3/2}$; the bending vibrations occur at order ϵ^2; and the vibrations of the bond between the hydrogen nucleus and its farther neighbor are of order $\epsilon^{5/2}$. In the standard Born-Oppenheimer approximation they all occur at order ϵ^2, and one must do a matrix diagonalization to find the normal modes of oscillation. Here they are automatically separated at the different orders.

For the specific example of $FHCl^-$, one easily sees that the vibrational energies are of the various different orders, although our model yields vibarional energies that are similar to those obtained by the standard Born–Oppenheimer harmonic approximation. We predict FH–Cl^- stretch, bending, and F–H stretch energies of 246 cm^{-1}, 875 cm^{-1}, and 2960 cm^{-1}, respectively. The corresponding experimental data are 275 cm^{-1}, 843 cm^{-1}, and 2710 cm^{-1}. We note that $246/875 \approx 0.281$ and $875/2960 \approx 0.296$ are both close to the physical $\epsilon^{1/2} \approx 0.287$. Thus, these energies are consistent with their appearing in our approach at orders $\epsilon^{5/2}$, ϵ^2, and $\epsilon^{3/2}$, respectively.

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Numerical Tensor Calculus

Wolfgang Hackbusch

1. Tensor Spaces

Given vector spaces V_j ($1 \leq j \leq d$), there is a unique (algebraic) tensor space $\mathbf{V} = \bigotimes_{j=1}^{d} V_j$. For instance, for $V_j = \mathbb{R}^{n_j}$ the elementary tensors $\mathbf{v} = \bigotimes_{j=1}^{d} v^{(j)}$ with $v^{(j)} \in \mathbb{R}^{n_j}$ are defined by $\mathbf{v}[i_1 \ldots i_d] = \prod_{j=1}^{d} v^{(j)}[i_j]$. The tensor space is defined by all (finite) linear combinations of elementary tensors. The dimension of $\mathbf{V}$ is $N := \prod_{j=1}^{d} n_j$.

Here we consider cases, where it is impossible to store all N entries. Examples may be $n_j = 1000$ and $d = 1000$ yielding $N = 1000^{1000}$ as well as the natural dimension $d = 3$ with $n_j = 10^6$. The latter example describes a grid function on a fine 3D-grid.

If the generating vector spaces $V_j = \mathbb{R}^{n_j \times n_j}$ are matrix spaces, the tensor product is also called Kronecker product and produces matrices of size $N \times N$.

For infinite dimensional functions spaces V_j, say for uni-variate functions in x_j, the tensor product yields d-variate functions $\mathbf{v}(x_1 \ldots x_d) = \prod_{j=1}^{d} v^{(j)}(x_j)$. Fixing a suitable norm on $\mathbf{V}$, the completion of the algebraic tensor space produces the topological tensor space.

2. Representation of Tensors

Since for huge N the tensors cannot be described by all their entries, one needs a data-sparse representation. Examples are the r-term format (canonical format)

$$\text{(1)} \qquad \mathbf{v} = \sum_{\nu=1}^{r} v_{\nu}^{(j)} \quad \text{for some } v_{\nu}^{(j)} \in V_j$$

and the tensor subspace format (Tucker format)

$$\text{(2)} \qquad \mathbf{v} = \sum_{i_1=1}^{r_1} \cdots \sum_{i_d=1}^{r_d} \mathbf{a}[i_1 \ldots i_d] b_{i_1}^{(1)} \otimes \ldots \otimes b_{i_d}^{(d)} \quad \text{for some } b_{i_1}^{(j)} \in V_j.$$

Fixing the representation rank $r \in \mathbb{N}$ in (1) and the vector-valued rank $\mathbf{r} = (r_1 \ldots r_d)$ in (2), we obtain the sets $\mathcal{R}_r$ and $\mathcal{T}_{\mathbf{r}}$. If $n_j \leq n$, any $\mathbf{v} \in \mathcal{R}_r$ require a storage of drn. For moderate r, this is feasable also for $d = n = 1000$. The hope is that tensors of large or even infinite rank can be approximated in $\mathcal{R}_r$ for moderate r. This is confirmed by the following example.

The function $1/\sqrt{t}$ can be approximated in any interval $[\eta, \infty)$ by exponential sums $E_r(t) := \sum_{\nu=1}^{r} \omega_\nu \exp(-\alpha_\nu t)$ (see [1]) such that the accuracy improves exponentially with r. For instance, $\left\| 1/\sqrt{\cdot} - E_r \right\|_{\infty, [1, \infty)} =: \varepsilon_r \leq 8^{3.5} \exp(-\pi \sqrt{r/2})$.

Substituting the Euclidean norm $t = \|x\|^2$ of $x \in \mathbb{R}^d$, we obtain an approximation of $1/\|x\|$ by $E_r(\|x\|^2) = \sum_{\nu=1}^{r} \omega_\nu \prod_{j=1}^{d} \exp(-\alpha_\nu |x_j|^2)$ which belongs to $\mathcal{R}_r$. This fact can be expoited for the convolution with the Colomb potential:

$$\left\| \int_{\mathbb{R}^3} \frac{f(y)dy}{\|\cdot - y\|} - \int_{\mathbb{R}^3} E_r(\|\cdot - y\|^2)f(y)dy \right\|_{\infty, \mathbb{R}^3} \leq 3.5 \sqrt[3]{\|f\|_{L^1}^2 \|f\|_{L^\infty}} \, \varepsilon_r^{2/3}.$$

However, both formats mentioned above have certain disadvantages. A better approach is the hierarchical tensor format $\mathcal{H}_{\mathbf{r}}$ (cf. [6], [5]). The hierarchy is given by a certain dimension partition tree. If this tree is chosen as linear tree (maximal depth), one obtains the so-called tensor-train format (cf. [9]). Even earlier, the latter format has been used in quantum physics (cf., e.g., [10]) and is named 'matrix product states' (MPS).

An important question concerns the closedness of the sets $\mathcal{R}_r$, $\mathcal{T}_{\mathbf{r}}$, and $\mathcal{H}_{\mathbf{r}}$, since for optimisation problems we build sequences $\mathbf{v}_\nu \in \mathcal{F}$ ($\mathcal{F} \in \{\mathcal{R}_r, \mathcal{T}_{\mathbf{r}}, \mathcal{H}_{\mathbf{r}}\}$) and want to know whether $\lim \mathbf{v}_\nu \in \mathcal{F}$. In fact, $\mathcal{T}_{\mathbf{r}}$ and $\mathcal{H}_{\mathbf{r}}$ are closed (even weakly closed), but $\mathcal{R}_r$ is not (cf. [5]). As mentioned before, the hierarchical tensor format $\mathcal{H}_{\mathbf{r}}$ is structured by a tree. In quantum physics one likes to replace trees by general graphs. In this case, however, the set is not closed.

3. Tensor Operations and Truncation

There are various operations between tensors, one may like to compute. We start with a simple example. Let $V_j = \mathbb{R}^{n_j}$. The Hadamard product $\odot : V_j \times V_j \to V_j$ is the entrywise multiplication: $(v \odot w)_i = v_i w_i$, which easily generalises to tensors. The property

$$\left(\bigotimes_{j=1}^{d} v^{(j)} \right) \odot \left(\bigotimes_{j=1}^{d} w^{(j)} \right) = \bigotimes_{j=1}^{d} \left(v^{(j)} \odot w^{(j)} \right)$$

allows to reduce this operation to the vector spaces V_j. However, if $\mathbf{v}, \mathbf{w} \in \mathcal{R}_r$ involve r terms, the product consists of r^2 terms:

$$\left(\sum_{\nu=1}^{r} v_\nu^{(j)} \right) \odot \left(\sum_{\mu=1}^{r} w_\mu^{(j)} \right) = \sum_{\nu=1}^{r} \sum_{\mu=1}^{r} \bigotimes_{j=1}^{d} \left(v_\nu^{(j)} \odot w_\mu^{(j)} \right).$$

This is a typical feature which requires a truncation step, by which one tries to approximate the result by an expression involving fewer terms. Further operations

are the addition, convolution, matrix-vector and matrix-matrix multiplication and the scalar product.

The truncation within $\mathcal{R}_r$ (possibly with regularisation) is not so easy (cf. [2]), whereas for the hierarchical format $\mathcal{H}_{\mathfrak{r}}$ the truncation can be based on several singular value decompositions (cf. [6]).

4. Tensorisation

The translation of a vector into a tensor is called 'tensorisation' (cf. [5]). The simplest case is a vector $v \in \mathbb{R}^n$ with $n = 2^d$. Then $\mathbb{R}^n$ is isomorphic to the tensor space $\mathbf{V} := \bigotimes_{j=1}^{d} \mathbb{R}^2$. The concrete isomorphism is

$$
\begin{array}{cccc}
\Phi_n : & \mathbf{V} & \to & \mathbb{R}^n \\
 & \mathbf{v} & \mapsto & v \qquad \text{with } v_k = \mathbf{v}[i_1 \cdots i_d] \text{ for } k = \sum_{j=1}^{d} i_j 2^{j-1}, 0 \le i_j \le 1.
\end{array}
$$

The tensor $\mathbf{v}$ may be represented by the tensor train representation [8] (see also [7]). The exact tensor representation is usually not interesting, since it requires the same storage n. Instead, one looks for an approximate tensor using the truncation procedure mentioned above.

If $v \in \mathbb{R}^n$ represents a smooth function on a grid with n point, one observes that the corresponding (approximate) tensor requires much less data. Typically, piece-wise smooth functions allow to reduce n to $O(\log(n))$. The analytic background is given in [3]. In fact, the tensorisation corresponds to a multi-scale approach.

Operations can be applied directly to the tensorised vectors (instead to the vectors). For instance, convolution of two n-vectors which correspond to tensors of size $O(\log(n))$, can be performed with $O(\log(n))$ arithmetical operations (cf. [4]).

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On the mixed regularity of electronic wavefunctions

Harry Yserentant

Atoms and molecules are physically described by the Schrödinger equation for a system of charged particles that interact by Coulomb attraction and repulsion forces. As the nuclei are much heavier than the electrons, the electrons almost instantaneously follow their motion. Therefore it is usual in quantum chemistry to separate the motion of the nuclei from from that of the electrons, that is, to look for the eigenvalues and eigenfunctions of the electronic Schrödinger operator

$$H = -\frac{1}{2}\sum_{i=1}^{N}\Delta_i - \sum_{i=1}^{N}\sum_{\nu=1}^{K}\frac{Z_\nu}{|x_i - a_\nu|} + \frac{1}{2}\sum_{\substack{i,j=1\\i\neq j}}^{N}\frac{1}{|x_i - x_j|}$$

written down here in dimensionless form or atomic units. It acts on functions with arguments $x_1,\ldots,x_N \in \mathbb{R}^3$, the coordinates of given N electrons. The positions $a_1,\ldots,a_K \in \mathbb{R}^3$ of the nuclei are kept fixed. The positive values Z_ν are the charges of the nuclei in multiples of the electron charge. This talk was concerned with the mixed regularity of these eigenfunctions and its implications for the complexity of the quantum-mechanical N-electron problem.

To state our regularity results, we need to introduce a scale of norms that is defined in terms of Fourier transforms. These norms are given by the expression

$$\|u\|_{\vartheta,m}^2 = \int \left\{1 + \sum_{i=1}^{N}|\omega_i|^2\right\}^m \left\{\prod_{i=1}^{N}\left(1 + |\omega_i|^2\right)\right\}^{\vartheta} |\widehat{u}(\omega)|^2 \, \mathrm{d}\omega.$$

They are defined on the Hilbert spaces $H_{\mathrm{mix}}^{\vartheta,m}$ that consist of the square integrable functions from $(\mathbb{R}^3)^N$ to $\mathbb{R}$ or $\mathbb{C}$ with Fourier transforms

$$\widehat{u} : (\mathbb{R}^3)^N \to \mathbb{C} : (\omega_1,\ldots,\omega_N) \to \widehat{u}(\omega_1,\ldots,\omega_N)$$

for which these expressions remain finite; $|\omega_i|$ is the euclidian norm of ω_i. The index m determines the isotropic smoothness, and the index ϑ the degree of mixed regularity. For nonnegative integer values m and ϑ, the norms measure the L_2-norm of weak partial derivatives. The spaces L_2 and H^1 belong to the class of these spaces. Our main result [KY] is that the eigenfunctions u of the electronic Schrödinger operator for eigenvalues below the essential spectrum are contained in

$$H_{\mathrm{mix}}^{1,0} \cap \bigcap_{\vartheta < 3/4} H_{\mathrm{mix}}^{\vartheta,1}.$$

In the general case, the bound $3/4$ can neither be completely reached nor improved further. An exception are systems of electrons of the same spin, for which the wavefunctions are completely antisymmetric under the exchange of the positions of the electrons and vanish at the singular points of the electron-electron interaction potential. The proof is based on a multiplicative splitting [Y2] of the wavefunctions into an explicitly known factor depending on the interelectronic distances and a more regular part in $H_{\mathrm{mix}}^{1,1}$ and utilizes techniques from interpolation theory.

The eigenfunctions u for eigenvalues below the essential spectrum decay exponentially in the L_2-sense. There exists a constant $\gamma > 0$ such that the function

$$x \;\to\; \exp\left(\gamma \sum_{i=1}^{N} |x_i| \right) u(x),$$

is square integrable. This constant depends on the distance of the eigenvalue under consideration to the bottom of the essential spectrum. More details and references to the literature can be found in [Y1]. It has been shown in [Y2] that these exponentially weighted eigenfunctions admit the same kind of representation as the eigenfunctions themselves. Thus they share with them the described regularity properties [KY]. This can be used to study the expansion of the solutions into correspondingly antisymmetrized tensor products of three-dimensional eigenfunctions [Y1] or orthogonal wavelets [Z], for example. It turns out that the convergence rates of such expansions measured in terms of the number of basis functions involved surprisingly do not deteriorate with the number of electrons and remain comparable to those for a system of two electrons or even only one electron [Y1]. Therewith the curse of dimensionality is in some sense broken.

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The regularity of tensor product approximations in L^2 in dependence of the target function

André Uschmajew

The approximation of a square integrable function of many variables by a sum of products of functions of much fewer variables has been a prominent approach in many fields of theory and application for a long time, the simplest example being an expansion into a classical Fourier series. The need of such approximations can be motivated by the curse of dimensionality, which makes high-dimensional PDEs or eigenvalue problems intractable by standard discretization techniques.

There have been recent attempts [2] to establish a tensor calculus for such high-dimensional problems, which enters as a nonlinear ansatz into their formulation,

in order to break the curse of dimensionality. By nonlinear we mean that the the component functions u_k, v_k, w_k in an approximation of the form

$$f(x, y, z) \approx \sum_{k=1}^{r} u_k(x) v_k(y) w_k(z)$$

are not supposed to lie in a prescribed linear subspace or prescribed subset of basis functions of, say, L^2, but are entirely arbitrary. This is in contrast to the situation of, for instance, full CI calculations in quantum chemistry.

From a theoretical point of view, it would be desirable if such tensor product approximations meet certain regularity requirements of the underlying problem. In the case of quantum chemistry they should, for instance, lie in H^1 in order to represent orbital wave functions. The question is now, whether such regularity requirements have to be enforced, or may be automatically guaranteed. For the case of approximation in L^2 the pleasant, and somehow surprising answer is the following

Theorem 1. *Let $f \in H^s(\mathbb{R}^{n+m+l})$, $\operatorname{rank} f \geq r$. Assume that $u_k \in L^2(\mathbb{R}^n)$, $v_k \in L^2(\mathbb{R}^m)$, $w_k \in L^2(\mathbb{R}^l)$, $k = 1, 2, \ldots, r$, are a local minimzers of*

$$\left\| f - \sum_{k=1}^{r} u_k \otimes v_k \otimes w_k \right\|_0^2 = min,$$

that is,

$$\int \left| f(x, y, z) - \sum_{k=1}^{r} u_k(x) v_k(y) w_k(z) \right|^2 \mathrm{d}x \mathrm{d}y \mathrm{d}z = min.$$

Then $u_k \in H^s(\mathbb{R}^n)$, $v_k \in H^s(\mathbb{R}^m)$ and $w_k \in H^s(\mathbb{R}^l)$ for $k = 1, 2, \ldots, r$.

Here $\operatorname{rank} f$ denotes the minimal number of terms needed to write f as a sum of products (could be infinite). It is only for simplicity that products of three functions are considered.

The claim of the above theorem is quite interesting, since the minimization itself is performed in L^2 so that, in principle, the components u_k, v_k, w_k are allowed to be nonsmooth. The proof of the theorem can be found in [3]. The main observation is that, say u_k, satisfies a first-order optimality condition of the form

$$(1) \qquad u_k(x) = \int f(x, y, z) \phi_k(y, z) \, \mathrm{d}y \mathrm{d}z \quad \text{a.e.}$$

for some function $\phi_k \in L^2(\mathbb{R}^{m+l})$ (which depends on all v_k and w_k). Looking at such an integral equation, it is clear that the regularity of u_k depends only on the regularity of f with respect to the variable x. Consequently, the theorem could be made more precise by considering functions of anisotropic regularity [3].

One corollary that we found very intersting is the following:

Corollary 2. *If $f \in H^s(\mathbb{R}^{n+m+l})$ has rank $r < \infty$, then in every representation*

$$f = \sum_{k=1}^{r} u_k \otimes v_k \otimes w_k$$

the components u_k, v_k and w_k are in H^s.

Hence f possesses mixed derivatives up to order $3s$. This is an interesting interaction between the algebraic concept of rank and the analytic concept of smoothness.

One unsatisfactory aspect of the results is that no estimates on the Sobolev norms of the components, which are independent from the solution, can be given. In [3] a-posteriori estimates are discussed, where, say, $\|u_k\|_s$ is estimated in terms of f and all v_k and w_k.

Starting from relation (1), it is possible to obtain similar regularity results for (i) different types of tensor approximation, such as optimal subspace approximation, and (ii) different notions of regularity, such as classical differentiability, see [3].

Besides giving theoretical justification for a tensor calculus in PDEs, the regularity results might have some practical consequences as well. Maybe they can be used to construct efficient schemes to actually calculate such tensor approximations based on the information that the functions one is looking for are regular in a certain sense. At least, if such approximations are found they can be efficiently stored and compressed, making a tensor calculus more feasible, as it was for instance elaborated in [1].

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BOSSANOVA - A bond order dissection approach for efficient electronic structure calculations

FREDERIK HEBER

(joint work with Michael Griebel, Jan Hamaekers)

Fast computation of the electronic Schrödinger equation is still an open problem. In the context of ab-initio solving schemes with linear scaling in the number of nuclei, one considers the overlap matrix in a discrete basis set and sets components to zero for a given cut-off radius. The resulting sparsity extends to the other operator matrices as well and can be used to perform necessary matrix multiplications in linear time.

Finer control is obtained if the components are set to zero based on heuristics instead of by using a cut-off parameter. This information is plentifully available from chemistry, e. g. a bond information based distance criterion can be used as a heuristic.

Here, we look at linear scaling schemes for molecular systems. In the context of fragmentation methods, the set of nuclei is partitioned into subsets, either disjoint

or not. For the partitioning the bond information is usually taken into account. Energies and related expectation values are approximated via summation. Note that these fragmentation approaches are only successful in a localized setting, i.e. where an exponential decay of the electronic orbitals is present.

We attempt to understand these schemes in terms of complexity and derive a linear scaling property from the underlying operator eigenvalue equation, in Hilbert space with inner product $< \Psi, \Psi >= \int \Psi^*(x)\Psi(x)dx$,

$$(1) \qquad\qquad < \Psi, \mathbb{H}\Psi >= E < \Psi, \Psi > .$$

The electronic Hamilton operator $\mathbb{H}$ is

$$(2) \qquad\qquad \mathbb{H} = -\tfrac{1}{2}\sum_i^N \nabla_i^2 - \sum_\alpha^M \sum_i^N \frac{Z_\alpha}{|R_\alpha - r_i|} + \sum_{i<j}^N \frac{1}{|r_i - r_j|}.$$

We may split up this operator into a one-electron part

$$\mathbb{H}_1(i) = -\tfrac{1}{2}\nabla_i^2 - \sum_\alpha^M \frac{Z_\alpha}{|R_\alpha - r_i|},$$

and a two-electron part that consists of electron-electron interaction only,

$$\mathbb{H}_2(i,j) = \frac{1}{|r_i - r_j|},$$

such that

$$\mathbb{H} = \sum_i^N \mathbb{H}_1(i) + \sum_{i<j}^N \mathbb{H}_2(i,j).$$

Let us consider the following ansatz function due to Hartree [1], where $\{\phi_i\}_i^N$ is a set of spin-orbital[1] functions for the N electrons,

$$(3) \qquad\qquad \Psi = \phi_1(r_1) \cdot \ldots \cdot \phi_N(r_N) = \prod_{i=1}^N \phi_i(r_i).$$

Then we obtain for the total electronic energy $E = E_1 + E_2 = \frac{<\Psi, \mathbb{H}_1 + \mathbb{H}_2 \Psi>}{<\Psi, \Psi>}$

$$E_1 = \sum_i^N \int \phi_i^*(r_i)\mathbb{H}_1\phi_i(r_i)dr_i$$

$$E_2 = \sum_{i<j}^N \int \phi_i^*(r_i)\phi_j^*(r_j)\mathbb{H}_2\phi_i(r_i)\phi_j(r_j)dr_i dr_j,$$

where we have used that for all i: $\int \phi_i^*(r_i)\phi_i(r_i)dr_i = 1$.

As a second ansatz let us consider the usual Slater [2] determinant construct

$$(4) \qquad\qquad \Psi = (N!)^{-\frac{1}{2}} \det(\phi_1(r_1) \cdot \ldots \cdot \phi_N(r_N)),$$

---

[1]Note that we neglect spin here for the sake of clarity.

which results in the same one-particle energy term but a different two-particle energy term

$$E_2 = \sum_{i<k}^{N} \int \phi_i^*(r_i)\phi_k^*(r_k)\mathbb{H}_2(i,k)\phi_i(r_i)\phi_k(r_k)dr_i dr_k + \ldots$$

$$\ldots \sum_{i<k}^{N} \int \phi_i^*(r_i)\phi_k^*(r_k)\mathbb{H}_2(i,k)\phi_k(r_i)\phi_i(r_k)dr_i dr_k,$$

where we have used the orthonormality of the set $\{\phi_i\}_i^N$ that gives rise to the Slater-Condon rules.

Comparing the two-particle terms we note that the correct antisymmetry of the Slater determinant construct (4) has given rise to the so-called exchange term, which the simpler Hartree ansatz (3) can not capture.

Let us for a moment consider the more general case of a non-orthogonal set of spin-orbitals $\{\phi_i\}_i$ and let us look at the simple case of an expectation value of an operator that is not acting on any electron coordinate, e.g. an overlap integral $<\Psi, \Psi>$. Then, we realize that in the case of the Hartree ansatz (3) we obtain a single term,

$$\int \phi_1^*(r_1) \cdot \ldots \cdot \phi_N^*(r_N)\phi_1(r_1) \cdot \ldots \cdot \phi_N(r_N)dr_1 \ldots dr_N.$$

In the case of the Slater determinant construct (4) we obtain a sum of $N!$ terms,

$$\int \phi_1^*(r_1) \cdot \ldots \cdot \phi_N^*(r_N)\mathbb{A}\left\{\phi_1(r_1) \cdot \ldots \cdot \phi_N(r_N)\right\} dr_1 \ldots dr_N,$$

where $\mathbb{A}$ is the antisymmetrizer given as

$$\mathbb{A} = \sum_{\sigma \in S_N} \epsilon(\sigma)\sigma$$

and $\epsilon(\sigma)$ is the sign of the permutation σ, which is an element in the symmetric group S_N.

Neglecting the specifics of one-particle and two-particle operators present in (2), the question is then: Are all these $N!$ terms necessary to compute the exchange term accurately? Or can we neglect terms based on some heuristic criterion such that in steps of $\mathbb{O}(N)$ this truncated sum converges to the true Hartree-Fock (HF) energy?

Initially, we have to consider $N!$ or approximately N^N terms. Let us take this determinant as a finite series over the possible permutations, ordered into levels consisting of all terms having equal number k of deranged elements. If we take just level $k = 0$, i.e. only the identity, we obtain the Hartree ansatz (3). If we take all $k = N$ levels, we obtain the Slater determinant construct (4). If all series terms are of the same order of magnitude, i.e. if the matrix is full, we are left with $\mathbb{O}(N^3)$ scaling due to matrix diagonalization. The magnitude however depends on the choice of the basis set, e.g. we have $\mathbb{O}(1)$ for an orthonormal set.
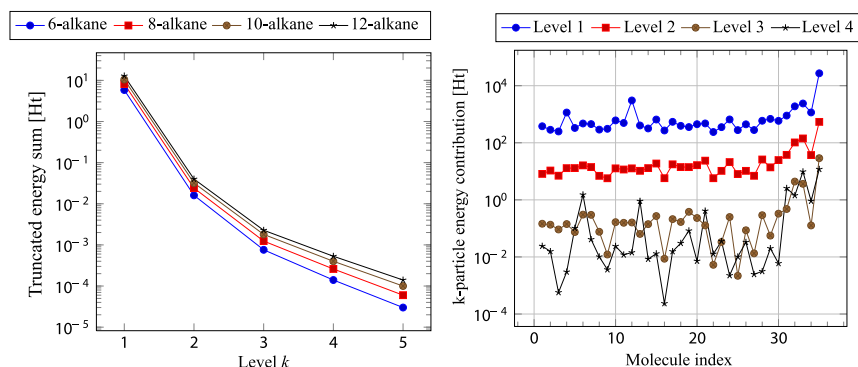
Assume we have something in between, namely the case of a hierarchy in the magnitude of the terms of the series. Let us take a closer look: We have $\mathbb{O}(N)$ levels and $(N-1)! \approx N^{(N-1)}$ terms per level. Let there be an upper bound $1 < \epsilon < 0$ for each overlap matrix element $\int \phi_k^* \phi_l dx$ with $k \neq l$. Each of the $N!$ terms of the determinant is associated to a specific permutation σ and thereby it has fixed points and deranged points. Fixed points relate to normalization integrals equal to one $- \int \phi_k^* \phi_k dx = 1$ – and deranged points to overlap integrals bound from above by ϵ. Each of the $N!$ terms can be placed into a hierarchy level based on powers of the bound ϵ which is related to the number k of deranged elements due to its associated permutation σ: each term on a level k has magnitude less than ϵ^k. Then we can estimate the sum over all terms per level k by

$$N^k \cdot \epsilon^k.$$

Thus, $\epsilon < \frac{1}{N}$ must hold in order to obtain a decay over the levels. That is the upper bound ϵ on the overlap depends on the total number of electron orbitals N, i.e. the system size. Here is where we need the locality of the wave function. It allows for a local environment around each orbital, containing N orbitals with an upper bound ϵ. Clearly, for a metallic system with delocalized orbitals, that are overlapping with many others, this scheme is not successful: If the environment contains more orbitals, the bound must be smaller. In our case of atomic orbitals this is clearly fulfilled by the exponential decay of the orbitals and the finite electron density. In our talk we investigated in detail various cases of such locality constraints on the overlap between orbitals and thus on the decay per level.

So far, we have considered only overlap and not the action of an operator, but the consequences in these more involved cases are very similar. Note that a clearer and more concise notation is given by density matrices and the extended Slater-Condon rules by Löwdin [3]. The essence is that we can re-distribute each term associated to a specific permutation to a specific set in a partition of the molecular system. Eventually, all terms belonging to such a set form the expectation value (1) with a full Slater determinant ansatz function (4) of the total ground state energy of another, smaller molecular system that consists only of atoms in this smaller set. If the partitioning scheme is linear in the number of sets, this eventually allows for a linear scaling, approximative, converging evaluation of the original molecular system's total ground state energy in terms of HF accuracy.

This truncated hierarchy and partitioning of the molecular system is basically the so-called Bond Order diSSection in an ANOVA-like fashion (BOSSANOVA) scheme, see [4]. Here, the fragmentation schemes are derived from the point of the ANalysis Of VAriance (ANOVA) decomposition of the Born-Oppenheimer-energy function working on nuclei coordinates. To this end, the system can easily be successfully built from one-particle energies, two-particle, namely bond energies, three-particle energies and so on, i.e. from the ANOVA terms of the energy. Our new approach is trivial to parallelize and gradients are obtained straightforwardly. Figures 1(a) and 1(b) underline experimentally the decay of the terms.

(a) Absolute error of summed fragmentary energies up to level k against full HF calculation for alkanes

(b) Sum over all terms associated to one-particle, two-particle, ... contributions to the total energy per level k for various organic molecules

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Tensor Decomposition in Electronic Structure Theory: Canonical Product Format and Coupled Cluster Theory

ALEXANDER A. AUER

(joint work with Udo Benedikt, Mike Espig, Wolfgang Hackbusch)

A series of new approximations for expressing tensorial quantities has been developed and refined in applied mathematics in recent years [1, 2]. These approaches are related to techniques like Cholesky decomposition, singular value decomposition or Laplace denominator decomposition [3, 4, 5, 6, 7] and yield low dimensional representations of high dimensional quantities. Especially appealing for applications in electronic structure theory is the canonical product format, where any tensor $A(w, x, y, z) \in \mathbb{R}^{n \times n \times n \times n}$ can be expressed as a sum over representing vectors connected by the Kronecker product:

$$\mathbf{A} = \sum_{r=1}^{R} (a^w)_r \otimes (a^x)_r \otimes (a^y)_r \otimes (a^z)_r$$

where R is the rank or expansion length of the approximation. To obtain a low rank approximation for a given tensor, an iterative scheme based on an accelerated gradient algorithm is utilised to find an approximate representation $\tilde{\mathbf{A}}$ with small rank and an upper bound for the error ϵ:

$$||\mathbf{A} - \tilde{\mathbf{A}}|| \leq \epsilon$$

In Coupled Cluster theory an exponential ansatz is used to express the Coupled Cluster wave function Ψ_{CC} based on the Hartree-Fock determinant Ψ_0:

$$|\Psi_{CC}\rangle = e^{\hat{T}}|\Psi_0\rangle$$

with the cluster operator

$$\hat{T} = \sum_{\substack{i \\ a}} t_i^a \hat{a}_a^+ \hat{a}_i + \sum_{\substack{ij \\ ab}} t_{ij}^{ab} \hat{a}_a^+ \hat{a}_i \hat{a}_b^+ \hat{a}_j + \ldots + \sum_{\substack{ij\ldots \\ ab\ldots}} t_{ij\ldots}^{ab\ldots} \hat{a}_a^+ \hat{a}_i \hat{a}_b^+ \hat{a}_j \ldots$$

The cluster operator can be truncated to give the hierarchy of CCSD (single t_i^a and double amplitudes t_{ij}^{ab}), CCSDT (also triples t_{ijk}^{abc} are included) and so on. [8] The energy can be obtained from the expectation value and the amplitudes are determined by projection:

$$\langle\Psi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Psi_0\rangle = E \qquad \langle\Psi_{ij\ldots}^{ab\ldots}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Psi_0\rangle = 0$$

The bottleneck of these calculations are contractions of the cluster amplitudes t with the two electron integrals v. The most time consuming step in CCSD, for example, is the contraction :

$$r_{ij}^{ab} \leftarrow t_{ij}^{ef} v_{ef}^{ab} = \sum_{e,f}^{n} t_{ij}^{ef} v_{ef}^{ab}$$

with n being a measure of the number of orbitals (In the following we will also use N as a measure of the size of the system). If the two electron integrals and amplitudes are cast into canonical product format :

$$v_{ef}^{ab} \approx \sum_{r=1}^{R} (v^a)_r \otimes (v^b)_r \otimes (v^e)_r \otimes (v^f)_r \qquad t_{ij}^{ab} \approx \sum_{k=1}^{K} (t^a)_k \otimes (t^b)_k \otimes (t^i)_k \otimes (t^j)_k$$

the contraction can be rephrased as

$$\sum_{k=1}^{K} \sum_{r=1}^{R} \left(\sum_{e=1}^{n} (t^e)_k (v^e)_r\right) \left(\sum_{f=1}^{n} (t^f)_k (v^f)_r\right) (v^a)_r \otimes (v^b)_r \otimes (t^i)_k \otimes (t^j)_k$$

$$= \sum_{k=1}^{K} \sum_{r=1}^{R} \langle (t^e)_k, (v^e)_r \rangle \ \langle (t^f)_k, (v^f)_r \rangle \ (v^a)_r \otimes (v^b)_r \otimes (t^i)_k \otimes (t^j)_k$$

Accordingly, this format has the advantage that a tensor contraction can be carried out as a combination of scalar products and vector copies that scale at most as $n \cdot K \cdot R$, were K and R denote the rank of the two tensors and n denotes the length of the vectors (usually the orbital index).

This way, *any* contraction can be reduced to scalar product/copy operations that

scale as $n \cdot K \cdot R$ in contrast to the exponential scaling with N that for example a FCI calculation would exhibit.

Investigations for the decomposition of integrals and Coupled Cluster amplitudes have been carried out in which the scaling of the expansion length with system and basis set size has been investigated [9]. It is found that with a threshold in the l^2 norm of 10^{-2} for the two-electron integrals the ranks scale as $N^{2.5}$ for the AO integrals, between $N^{1.5}$ (v_{ij}^{ab}) and $N^{1.7}$ (v_{cd}^{ab}) for the MO integrals and as $N^{1.4}$ or better for the t_2 amplitudes as estimated from MP2. Thus, that the rank for the two-electron integrals scales approximately as N^2 while the rank of the wavefunction parameters scales a little higher or equal to N. As a consequence, for any post-HF electronic structure calculation an overall scaling in the order of N^4 or N^5 seems possible. Furthermore, the error of a low-rank approximation is bound such that the advantages of highly accurate post-HF methods are preserved. Typical errors resulting for the energy are in the order of less than a millihartree [9].

Besides the canonical product format other tensor formats might also have a high potential for the application in CI-bases approaches from electronic structure theory. Among these, the Matrix Product State representation that is frequently used in DMRG [10, 11, 12, 13, 14] might be of advantage:

$$\mathbf{A} = \sum_{k=1}^{K} \sum_{l=1}^{L} \sum_{r=1}^{R} (a^w)_k \otimes (a^x)_{kl} \otimes (a^y)_{lr} \otimes (a^z)_r$$

Another format arises naturally from a closer look at the RI approximation or Cholesky decomposition for the two electron integrals [15, 16, 17]

$$\langle pq| \, |rs\rangle = \sum_{x=1}^{X} V_{pq}^x V_{rs}^x$$

by application of the decomposition to the RI matrices, so that these matrices can be cast into canonical product format

$$V_{pq}^x = \sum_{k=1}^{K} (v^p)_k \otimes (v^q)_k \otimes (v^x)_k \qquad V_{rs}^x = \sum_{l=1}^{L} (v^r)_l \otimes (v^s)_l \otimes (v^x)_l$$

which then yields the following form when the two electron integrals are reconstructed

$$\langle pq| \, |rs\rangle = \sum_{x=1}^{X} \sum_{k=1}^{K} \sum_{l=1}^{L} (v^p)_k \otimes (v^q)_k \otimes (v^x)_k \otimes (v^r)_l \otimes (v^s)_l \otimes (v^x)_l$$

$$= \sum_{k=1}^{K} \sum_{l=1}^{L} \mathbf{X}_{kl} \, (v^q)_k \otimes (v^x)_k \otimes (v^r)_l \otimes (v^s)_l$$

This format might be used to circumvent the increase of rank in subsequent tensor contractions. All of these are subject to current research and further possibilities will be explored for finding appropriate approximations for post-HF electronic

structure methods.

From these results we conjecture that using low rank approximations for the wavefunction parameters solving the Schrödinger equation numerically is possible in sub-exponential complexity. This perspective is almost like reaching a promised land, as indications for the possibility of such a scheme exist in several forms (Hohenberg-Kohn Theorems of DFT, modern versions of Quantum Monte Carlo or DMRG etc.).

Certainly, with new techniques from numerical mathematics at hand we seem to have reached at least some kind of shore. But while this might be the El Dorado quantum chemists have been looking for it might just as well be some strange small island that will soon be forgotten after we have left it for the next big finding. And just as for any discovery, the problems start immediately after reaching the shore - a long list of questions needs to be addressed, and several criteria have to be fulfilled for a practicable scheme:

- Is the decomposition of the tensorial quantities feasible as far as computational effort is concerned ?
- How to minimise the effort for the decomposition procedure ?
- Is the procedure numerically stable ?
- Is the canonical format really optimal and what other options do we have ?

And thinking even further (in the direction of matrix product states in DMRG) - if one would not introduce the canonical format as an a-posteriori approximation scheme for multidimensional quantities but rather as an ansatz in the Hamiltonian, what new view on electronic structure methods would evolve from this ?

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A numerical analysis for the Coupled Cluster equations

THORSTEN ROHWEDDER

Nowadays, the Coupled Cluster (CC) method is the probably most widely used high precision method for the solution of the main equation of electronic structure calculation, the *stationary electronic Schrödinger equation*. Traditionally, the equations of CC are formulated as a nonlinear approximation of a Galerkin solution of the electronic Schrödinger equation, i.e. within a given finite basis set. Unfortunately, this concept prohibits the direct application of concepts of nonlinear numerical analysis to obtain e.g. existence and uniqueness results, quasi-optimality estimates, or results on the convergence of discrete solutions to the full solution. The solution presented in this talk is the equivalent reformulation of the original, continuous electronic Schrödinger equation as a root equation for an infinite-dimensional nonlinear Coupled Cluster function, discretizations of which then lead to the canonical projected CC equations. The main obstacle is that the cluster operator T and its adjoint have to be continuous mappings on the energy space $\mathbb{H}^1$. Once this is proven, one can formulate the continuous CC equations and define the continuous CC function f, to which then modifications of well-known concepts from nonlinear operator analysis can be applied: We prove that f possesses the property of being locally Lipschitz continuous and locally strongly monotone in a neighborhood of the solution t^*; then, techniques from operator theory partly already used in [4] apply to obtain existence/uniqueness and convergence results, and we will prove a goal oriented error estimator [1] for convergence of the energy E^*.

The (continuous as well as the classical, discrete) Coupled Cluster method is based on a fixed one-particle basis

$$B := \{\chi_P \mid P \in \mathcal{I}\} \subseteq H^1(\mathbb{R}^3 \times \{\pm\tfrac{1}{2}\})$$

($\mathcal{I}$ infinite for continuous CC, finite otherwise), which is used to construct an antisymmetric basis

$$(1) \qquad \mathbb{B} := \{\Psi_\mu \mid \mu \in \mathcal{M}\}, \qquad \Psi_\mu := \bigwedge_{i=1}^{N} \chi_{P_i} := \mathcal{Q}(\otimes_{i=1}^{N}\chi_{P_i}),$$

in which $\mathcal{Q} : L^2((\mathbb{R}^3 \times \{\pm\tfrac{1}{2}\})^N) \to L^2((\mathbb{R}^3 \times \{\pm\tfrac{1}{2}\})^N)$ is the antisymmetrization mapping. $\mathbb{B}$ is indexed by a set $\mathcal{M}$ of multiindices, each consisting of N ordered indices from $\mathcal{I}$, and spans the solution space $\mathbb{H}^1$ of antisymmetric, one time weakly differentiable functions, on which the electronic Schrödinger equation

$$(2) \qquad\qquad \langle \Phi,\ H\underline{\Psi} \rangle \ = \ E\langle \Phi,\ \underline{\Psi} \rangle \text{ for all } \Phi \in \mathbb{H}^1,$$

is to be solved. To formulate a set of CC equations equivalent to (2), i.e. where $\mathcal{I}$ is infinite, we assume the following: A subset

$$(3) \qquad B_{\text{occ}} := \{\chi_{I_1}, \ldots, \chi_{I_N}\} \subseteq B$$

of N basis functions from B is a basis of an N-dimensional invariant subspace of a linear symmetric operator $F : H^1 \to H^{-1}$; this operator F is spectrally equivalent to the canonical H^1-inner product $\langle \cdot, \cdot \rangle_1$, i.e. there are $\gamma, \Gamma > 0$ such that

$$\gamma \, \langle \varphi, \varphi \rangle_1 \; \leq \; \langle F\varphi, \varphi \rangle \; \leq \; \Gamma \, \langle \varphi, \varphi \rangle_1 \quad \text{for all} \quad \varphi \in H^1(\mathbb{R}^3 \times \{\pm\tfrac{1}{2}\}).$$

With this assumption, the formalism of excitation operators X_μ, central to the Coupled Cluster ansatz, can now be extended to the infinite dimensional setting, in particular to the space $\mathbb{H}^1$. We define the reference determinant Ψ_0 as the determinant formed via (1) from the orbitals contained in B_{occ}. Further, we define for each multiindex $\mu = (I_{r+1}, \ldots, I_N, A_1, \ldots, A_r) \in \mathcal{M}$ an excitation operator X_μ by its action on $\Psi_\nu \in \mathbb{B}$: If the index ν contains the indices $I_1, \ldots, I_r$, the operator replaces them by the orbitals $A_1, \ldots, A_r$; otherwise, we let $X_\mu \Psi_\nu = 0$. There then holds the following important theorem.

Theorem 1. *(Continuity of the cluster operator.) Let $T = \sum_{\alpha \in \mathcal{M}^*} t^* X_\alpha$ be the cluster operator mapping the reference determinant Ψ_0 to $\Psi^* = \sum_{\alpha \in \mathcal{M}^*} t_\alpha \Psi_\alpha \in \mathbb{H}^1$. T and its $\mathbb{L}^2$-adjoint $T^\dagger$ map $\mathbb{H}^1 \to \mathbb{H}^1$ boundedly; there holds*

$$(4) \qquad \|T\|_{\mathbb{H}^1 \to \mathbb{H}^1} \; \sim \; \|\Psi^*\|_{\mathbb{H}^1} \; \sim \; \|t^*\|_{\mathbb{V}} \qquad \|T^\dagger\|_{\mathbb{H}^1 \to \mathbb{H}^1} \; \leq \; \|\Psi^*\|_{\mathbb{H}^1},$$

in which $\| \cdot \|_{\mathbb{V}}$ denotes a norm on weighted coefficient space $\mathbb{V} \subseteq \ell_2$, isomorphic to $\mathbb{H}^1$.

From this result, we can deduce the following:

Theorem 2. *(The continuous Coupled Cluster equations.) A function $\underline{\Psi} = \Psi_0 + \Psi^* \in \mathbb{H}^1$ with $\Psi_0 \perp \Psi^*$, together with a corresponding eigenvalue $E^* \in \mathbb{R}$ solves the (weak, CI) eigenproblem*

$$(5) \qquad \langle \Psi_\mu, \, (H - E^*)\underline{\Psi} \rangle \; = \; 0, \text{ for all } \mu \in \mathcal{M}$$

if and only if $\underline{\Psi} = e^T \Psi_0$ for some cluster operator $T = \sum_{\alpha \in \mathcal{M}^*} t_\alpha X_\alpha$ for which $\|t_\alpha\|_{\mathbb{V}} < \infty$, and which fulfils the (continuous) linked Coupled Cluster equations,

$$(6) \qquad E^* \; = \; \langle \Psi_0, He^T \Psi_0 \rangle, \; \langle \Psi_\mu, e^{-T} He^T \Psi_0 \rangle = 0, \text{ for all } \mu \in \mathcal{M}^*,$$

that is, if $t^* := (t_\alpha)_{\alpha \in \mathcal{M}^*} \in \mathbb{V}$ fulfils the root equation for the Coupled Cluster function

$$(7) \qquad f : \mathbb{V} \; \to \; \mathbb{V}', \; f(t) := \big(\langle \Psi_\alpha, e^{-T} He^T \Psi_0 \rangle \big)_{\alpha \in \mathcal{M}^*} \; = \; 0 \in \mathbb{V}'.$$

Now, Galerkin-discretization of the nonlinear equation (7), being basically equivalent to the electronic Schrödinger equation, yields the classical, projected CC equations, and their connection to the continuous solution t^* can directly be analyzed by investigating the analytical properties of the CC function given in the following.

Theorem 3. *(Strong monotonicity.) The CC function f and all derivatives $f^{(n)}$ of f are Lipschitz-continuous on bounded domains of $\mathbb{V}$.*

Let E^* be a simple eigenvalue of H. If the reference determinant Ψ_0 lies in a suitable neighbourhood of the (intermediately normed) solution $\underline{\Psi}$ of the Schrödinger equation, the Coupled Cluster function f is strongly monotone in a neighbourhood of its solution $t^* = (t^*_\alpha)_{\alpha \in \mathcal{M}^*}$, i.e. there are constants $\gamma, \delta > 0$ such that

$$(8) \qquad \langle f(s) - f(t), s - t \rangle \ \geq \ \gamma \cdot \|s - t\|_{\mathbb{V}}^2$$

holds for all $s, t \in \mathbb{V}$ with $\|s - t^*\|_{\mathbb{V}}, \|t - t^*\|_{\mathbb{V}} < \delta$.

The main quatities that influence the constant γ are the quality of the reference determinant Ψ_0 and the spectral gap of the Hamiltonian. From the above theorem, one obtains the existence and uniqueness statements and error estimates for the CC method compiled in the following.

Theorem 4. *(Existence and uniqueness.) The solution t^* of the Coupled Cluster function that belongs to the lowest eigenvalue of (2) is unique in the neighbourhood $B_\delta(t^*)$.*

Let $\mathbb{V}_d$ be a subspace of $\mathbb{V}$ for which $d(t^*, \mathbb{V}_d) := \min_{v \in \mathbb{V}_d} \|v - t^*\|_{\mathbb{V}}$ is sufficiently small. Then the discretised (projected) problem

$$(9) \qquad \langle f(t_d), v_d \rangle \ = \ 0 \text{ for all } v_d \in \mathbb{V}_d$$

admits a solution t_d in $B_{\delta,d} := \mathbb{V}_d \cap B_\delta(t^*)$ which is unique on $B_{\delta,d}$ and fulfils the quasi-optimality estimate

$$(10) \qquad \|t_d - t^*\|_{\mathbb{V}} \ \leq \ \frac{L}{\gamma} \, d(t^*, \mathbb{V}_d)$$

with L the Lipschitz constant and γ the monotonicity constant of f on $B_\delta(t^*)$. In particular, if $\mathbb{V}_{(n)}$ is a sequence of subspaces of $\mathbb{V}$ for which $\lim_{n \to \infty} d(t^*, \mathbb{V}_{(n)}) \to 0$, the corresponding solutions $t_{(n)} \in B_{\delta,(n)}$ of (9) converge to the continuous solution $t^* \in \mathbb{V}$.

From strong monotonicity, one can also obtain estimators for the CC energy. To this end, we follow [1] in considering the stationary points of the Lagrangian $\mathcal{L}(t, z) = E(t) + \langle f(t), z \rangle$, i.e. (t^*, z^*) that solves

$$(11) \quad \mathcal{L}'(t^*, z^*) = \left\{ \begin{array}{c} \langle E'(t^*), s \rangle - \langle Df(t^*)s, z^* \rangle \\ \langle f(t^*), s \rangle \end{array} \right\} = 0 \qquad \text{for all } s \in \mathbb{V}.$$

We obtain the following results.

Theorem 5. *(Energy estimators.) Denote by (t^*, z^*) and (t_d, z_d) the solutions the Coupled Cluster equations (11) and of the discretised (projected) Coupled Cluster equations on $\mathbb{V}_d$, a sufficiently large subspace of $\mathbb{V}$ in the sense that for $d(\mathbb{V}_d, t^*)$, $d(\mathbb{V}_d, z^*) < c$ for a suitable $c > 0$, and Under the assumptions of Theorem 3, there holds*

$$|E(t^*) - E(t_d)| \ \leq \ \|t_d - t^*\|_{\mathbb{V}} \left(c_1 \, \|t_d - t^*\|_{\mathbb{V}} \ + \ c_2 \, \|z_d - z^*\|_{\mathbb{V}} \right),$$

$$|E(t^*) - E(t_d)| \ \lesssim \ \big(\, d(\mathbb{V}_d, t^*) \ + \ d(\mathbb{V}_d, z^*) \, \big)^2.$$

where the above constants are specified in the proof.

We thus obtain for the CC method a variety of existence and uniqueness statements, quasi-optimality results and error estimates results that resemble much those for the simpler CI (Galerkin) method (2), while the Lagrangian approach, via which the dual solution z^* enters, pays respect to the fact that CC is non-variational. The main constants influencing the performance of the CC method are (i) the quality of the reference determinant Ψ_0 and (ii) the gap between the lowest eigenvalue and the rest of the spectrum of the Hamiltonian.

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Bridging the gap between quantum Monte Carlo and explicitly correlated methods

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(joint work with Sambasiva Rao Chinnamsetty, Hongjun Luo, André Uschmajew)

It is a major goal in quantum chemistry to achieve highly accurate approximate solutions of the electronic Schrödinger equation in the Born-Oppenheimer approximation. The conventional approach based on Slater determinants suffers from slow convergence with respect to the underlying single particle basis. To overcome this problem, additional basis functions explicitly depending on inter-particle distances were introduced by Kutzelnigg and Klopper [1, 2] together with sophisticated approximation schemes to keep the additional computational effort under control. A large variety of these pair-correlation functions have been discussed in the literature, cf. [3] and references therein. We want to study a generalized approach based on fully optimized pair-correlation functions using stochastic techniques commonly employed in *quantum Monte Carlo* (QMC) calculations and tensor product approximation to compute the required two- and three-electron integrals in an accurate and efficient manner. For a thorough discussion of our approach including numerical examples, we refer to a forthcoming publication [4].

The starting point of our approach is the Jastrow ansatz for the wavefunction, i.e., $\Psi = \mathcal{F}\Phi$, with Jastrow factor

$$\mathcal{F}(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \exp\left(\sum_i \tau^{(1)}(\mathbf{x}_i) + \sum_{i<j} \tau^{(2)}(\mathbf{x}_i, \mathbf{x}_j) + \cdots\right),$$

and Φ corresponds to the *Hartree-Fock* (HF) Slater determinant. This ansatz represents the most popular wavefunction for QMC calculations [5], where the pair-correlation function is typically represented by a symmetric polynomial

$$
(1) \qquad \tau^{(2)}(\mathbf{x}_i, \mathbf{x}_j) = \sum_{I,J} \sum_{l,m,n} c_{lmn}^{I,J} (\bar{r}_{iI}^m \bar{r}_{jJ}^n + \bar{r}_{jI}^m \bar{r}_{iJ}^n) \bar{r}_{ij}^l,
$$

in rational distance variables

$$
\bar{r}_{iI} = \frac{|\mathbf{x}_i - \mathbf{A}_I|}{1 + |\mathbf{x}_i - \mathbf{A}_I|} \quad \text{and} \quad \bar{r}_{ij} = \frac{|\mathbf{x}_i - \mathbf{x}_j|}{1 + |\mathbf{x}_i - \mathbf{x}_j|}.
$$

For electron-nucleus distance variables $\bar{r}_{iI}$ only even powers are usually taken into account. Efficient stochastic techniques for Jastrow factor optimization have been developed and applied to atoms, molecules and solids [6]. In the present work, we have used our iterative perturbative approach [7] which provides a stable and efficient optimization scheme.

After optimization, the pair-correlation function $\tau^{(2)}$ can serve as additional basis function

$$
w_{ij}(\mathbf{x}_1, \mathbf{x}_2) := (1 - Q_1)(1 - Q_2)\tau^{(2)}(\mathbf{x}_1, \mathbf{x}_2)\phi_i(\mathbf{x}_1)\phi_j(\mathbf{x}_2),
$$

in explicitly correlated methods. Here the indices i, j run over all occupied HF orbitals, and projection operators Q_1 and Q_2 map into the single-particle space spanned by occupied orbitals. In order to enable an efficient computation of the required two- and three-electron integrals, we try to find the best separable approximation of $\tau^{(2)}$ in $L_2(\mathbb{R}^6)$ for a given separation rank κ in the general form

$$
\tau^{(2)}(\mathbf{x}, \mathbf{y}) \approx \sum_{k=1}^{\kappa} u_k^{(1)}(x_1, y_1) u_k^{(2)}(x_2, y_2) u_k^{(3)}(x_3, y_3),
$$

which is known in the literature as the canonical tensor format [8].

To illustrate our tensor product approach let us consider a typical three-electron integral

$$
\sum_m \int_{\mathbb{R}^3} A_{jm}(\mathbf{x}_1)\phi_i(\mathbf{x}_1)\phi_k(\mathbf{x}_1)B_{ml}(\mathbf{x}_1)d^3x_1,
$$

with

$$
(2) \qquad A_{jm}(\mathbf{x}_1) := \int_{\mathbb{R}^3} |\mathbf{x}_1 - \mathbf{x}_2|^{-1}\phi_j(\mathbf{x}_2)\phi_m(\mathbf{x}_2)d^3x_2,
$$

$$
(3) \qquad B_{ml}(\mathbf{x}_1) := \int_{\mathbb{R}^3} \tau^{(2)}(\mathbf{x}_1, \mathbf{x}_3)\phi_m(\mathbf{x}_3)\phi_l(\mathbf{x}_3)d^3x_3,
$$

where indices i, j, k, l, m refer to occupied HF orbitals. For each pair of occupied orbitals, we first compute a low-rank approximation of their product

$$
(4) \qquad \phi_i(\mathbf{x})\phi_j(\mathbf{x}) \approx \sum_{k=1}^{\kappa'} \varphi_{ij,k}^{(1)}(x_1)\,\varphi_{ij,k}^{(2)}(x_2)\,\varphi_{ij,k}^{(3)}(x_3).
$$

With canonical tensor product approximations for the Coulomb potential and pair-correlation function at our disposal it is straightforward to compute their convolutions with orbital products, e.g.,

$$B_{ml}(\mathbf{x}) = \sum_{k,k'=1}^{\kappa,\kappa'} \prod_{i=1}^{3} \int_{\mathbb{R}} u_k^{(i)}(x_i, y_i) \varphi_{ml,k'}^{(i)}(y_i) dy_i.$$

In order to reduce storage requirements and simplify further computations, we perform additional compression steps for the intermediate quantities A_{jm} and B_{ml}. With it we can compute

$$(5) \qquad D_{jl}(\mathbf{x}) := \sum_m A_{jm}(\mathbf{x}) B_{ml}(\mathbf{x}) \approx \sum_{k=1}^{\kappa} d_{jl,k}^{(1)}(x_1)\, d_{jl,k}^{(2)}(x_2)\, d_{jl,k}^{(3)}(x_3),$$

including a further compression step. Finally, three-electron integrals are easily computed in the tensor format. A similar approach has been outlined in [9, 10] for the computation of standard two-electron integrals.

1. Best N-term approximation theory for tensor components

In order to perform computations in the tensor format in an efficient manner, it is beneficial to have data sparse representations for univariate and bivariate tensor components available.

The concept of best N-term approximation belongs to the realm of nonlinear approximation theory [11]. One considers for a given basis the best possible approximation of a function f in the nonlinear subset Σ_N which consists of all possible linear combinations of at most N basis functions. Here, the approximation error $\sigma_N(f) := \inf_{f_N \in \Sigma_N} \|f - f_N\|_H$ is given with respect to the norm of an appropriate Hilbert space H. Best N-term approximation spaces $A_q^\alpha(H)$ for a Hilbert space H can be defined such that a convergence rate $\sigma_N(f) \sim N^{-\alpha}$ with respect to the number of basis functions N can be achieved.

In our applications we consider best N-term approximation for wavelet bases. Since we are mainly interested in the energy of a molecule it is appropriate to restrict to the Sobolev space $H^1(\mathcal{I})$ on a bounded interval $\mathcal{I} \subset \mathbb{R}$. The corresponding approximation spaces $A_q^\alpha(H^1(\mathcal{I}))$ have been identified as Besov spaces [11] which have an equivalent norm for $\frac{1}{q} = \alpha + \frac{1}{2}$ in terms of weighted ℓ_q spaces of wavelet coefficients.

Best N-term approximation can be also applied to bivariate tensor components of pair-correlation functions, where the basis consists of anisotropic tensor product wavelets $\psi_{j_1,a_1}(x)\, \psi_{j_2,a_2}(y)$, cf. [12]. Similar to the univariate case, we consider approximation spaces $A_q^\alpha(H^1(\Omega))$ for a square $\Omega := \mathcal{I} \times \mathcal{I} \subset \mathbb{R}^2$.

1.1. **Univariate components of tensor products.** In the course of our tensor algorithm for the computation of three-electron integrals, we encounter several intermediate quantities (2), (3), (4) and (5) which are represented by tensor product approximations.

Theorem 1. *Let the function η correspond to a solution ϕ_i of the Hartree-Fock equation, a pointwise product $\phi_i \phi_j$, its convolution with the Coulomb potential A_{lm} or pair-correlation function B_{lm}. The directional univariate components $\eta_k^{(i)}$, for $i = 1, 2, 3$ and $k = 1, \ldots, \kappa$, of their canonical best separable tensor product approximations, i.e., local minimizers[1]*

$$\sum_{k=1}^{\kappa} \eta_k^{(1)} \otimes \eta_k^{(2)} \otimes \eta_k^{(3)} = \arg \min_{\{h_k^{(i)}\}} \left\| \eta - \sum_{k=1}^{\kappa} h_k^{(1)} \otimes h_k^{(2)} \otimes h_k^{(3)} \right\|_{L_2(\mathbb{R}^3)},$$

belong to best N-term approximation spaces $A_q^\alpha(H^1(\mathcal{I}))$ for all $\alpha > 0$ and $\frac{1}{q} = \alpha + \frac{1}{2}$.

1.2. **Bivariate tensor components of pair-correlation functions.** In order to study the best N-term approximation of bivariate tensor components of a pair-correlation function, it is necessary to estimate its singular behaviour along the diagonal. No rigorous general results are presently available, however, guided by the ansatz (1) used in QMC calculations, we make the following assumption

$$(6) \qquad |\partial_{x_i}^p \tau^{(2)}(\mathbf{x}, \mathbf{y})| \lesssim |\mathbf{x} - \mathbf{y}|^{1-p} f(\mathbf{x}, \mathbf{y}), \quad \text{for } p \geq 1 \text{ and } \mathbf{x} \neq \mathbf{y},$$

concerning the singular behaviour of the pair-correlation function near the diagonal, where f belongs to the Schwartz space $\mathcal{S}(\mathbb{R}^3 \times \mathbb{R}^3)$ of smooth rapidly decreasing functions.

Theorem 2. *Suppose a two-particle correlation function $\tau^{(2)}$ satisfies the estimate (6). The bivariate components $u_k^{(i)}(x_i, y_i)$, $i = 1, 2, 3$, $k = 1, \ldots, \kappa$, of a canonical tensor product approximation, i.e., a local minimizer*

$$\sum_{k=1}^{\kappa} u_k^{(1)} \otimes u_k^{(2)} \otimes u_k^{(3)} = \arg \min_{\{w_k^{(i)}\}} \left\| \tau^{(2)} - \sum_{k=1}^{\kappa} w_k^{(1)} \otimes w_k^{(2)} \otimes w_k^{(3)} \right\|_{L^2(\mathbb{R}^6)},$$

belong to best N-term approximation spaces $A_q^\alpha(H^1(\Omega))$ with $0 < \alpha < \frac{3}{2}$ and $\frac{1}{q} = \alpha + \frac{1}{2}$ for anisotropic tensor product wavelets.

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Multiparticle equations for interacting Dirac Fermions in graphene nanostructures

HEINZ SIEDENTOP

(joint work with Reinhold Egger, Alessandro De Martino, and Edgardo Stockmeyer)

We study the energy of quasi-particles in graphene within the Hartree-Fock approximation. The quasi-particles are confined via an inhomogeneous magnetic field and interact via the Coulomb potential. We show that the associated functional has a minimizer and determine the stability conditions for the N-particle problem in such a graphene quantum dot. See [1].

This work has been continued by Paananen, Egger, and Siedentop [2]. There, the ground state energy is computed as a function of the effective interaction parameter α from the Hartree-Fock approximation and, alternatively, by employing the Müller exchange functional. For $N = 2$, we compare those approximations to exact diagonalization results. The Hartree-Fock energies are highly accurate for the most relevant interaction range of α up to about 2, but the Müller functional leads to an unphysical instability when α exceeds 0.756. Up to 20 particles were studied using Hartree-Fock calculations. Wigner molecule formation was observed for strong but realistic interactions, accompanied by a rich peak structure in the addition energy spectrum.

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Atomic Structure via Highly Charged Ions

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(joint work with Gero Friesecke)

The principal aim of quantum chemistry is to solve the (non-relativistic, Born-Oppenheimer) electronic Schrödinger equation (SE). In principle, this allows the prediction of all chemical and physical properties of the system. However, due to the dimension scaling exponentially with the number of particles, standard numerical techniques are unsuitable, and an approximate model must be treated. In addition, this is a tough multi-scale problem; interest lies not in absolute energies, but in energy differences, which are generally several orders of magnitude smaller.

Although very successful, most numerical methods in current use are based on chemical intuition and computational experience. In addition, the best calculated wavefunctions are linear combinations of millions or even billions of Slater determinants. This presents major problems when trying to analyse such wavefunctions, or to interpret them in terms of standard chemistry models, such as orbital shell filling (the Aufbau principle).

We consider iso-electronic sequences in which the number of electrons N is kept fixed and the nuclear charge Z is increased, leading to highly-charged ions. The mathematical motivation is that the ratio between spectral gaps (differences in eigenvalues of the Hamiltonian) and the total energies (eigenvalues) becomes small in the large-Z limit: (spectral gaps)/(total energies)= $\mathcal{O}(1/Z)$. The true physical ratio is small, even for neutral atoms, e.g. 1:1000 for Carbon, leading to a truly multi-scale system.

We show that many of the interesting chemical properties of small atoms and ions can be demonstrated through the 'PT model', based on first order perturbation theory[1]. This model is symmetry preserving and produces numerically accurate results for highly charged ions. The central result is:

Theorem[1] Consider the SE for the atom/ion with N=1 to 10 electrons and nuclear charge Z.

(i) For sufficiently high Z, the PT model ground state (lowest eigenspace) angular momentum, spin and parity quantum numbers, and its dimension agree with that of the SE. In practice, this holds for all $Z \geq N$.

(ii) The lowest $n(N)$ energy levels of the SE have the asymptotic expansion

$$\frac{E_j(N,Z)}{Z^2} = \tilde{E}^{(0)} + \frac{1}{Z}\tilde{E}_j^{(1)} + \mathcal{O}\left(\frac{1}{Z^2}\right) \text{ as } Z \to \infty,$$

where $\tilde{E}^{(0)}$ and $\tilde{E}_j^{(1)}$ are explicitly calculated rational numbers.

(iii) In the limit of highly charged ions ($Z \to \infty$), the SE and PT model ground state (a simple, explicit vector space) agree, in the sense that, in the operator norm, the projections P_0, $\tilde{P}_0$ onto these spaces satisfy $\lim_{Z \to \infty} \|P_0 - \tilde{P}_0\| = 0$.

The derivation requires a rescaling of the SE, standard techniques from degenerate perturbation theory, and a careful analysis of the symmetry group of the Hamiltonian and its representation theory. This analysis vastly simplifies

the problem, e.g. by decomposing the $70{\times}70$ dimensional matrix for Carbon into fifteen $2{\times}2$ and forty $1{\times}1$ matrices. Calculation of the high-dimensional (over $(\mathbb{R}^3 \times \mathbb{Z}_2)^N$) energy integrals is achieved through Slater's rules, Fourier analysis and residue calculus, leading to purely rational numbers. The whole process can be performed by hand; given the sizes of the matrices involved this is somewhat surprising. The resulting simple wavefunctions can be written out explicitly[1].

By suggesting a novel scaling in which to plot energies of iso-electronic sequences, this result allows identification of incorrectly assigned experimental results e.g. for five-electron ions[3]. It also allows, through curve fitting, to predict the values of missing experimental energy levels. In addition, some empirical chemical observations may be studied rigorously.

For example, for seven out of ten sequences (H, He, Li, N, O, F, Ne), the standard Born-Hund-Slater configuration (interpreted as a Slater determinant) is an element of the asymptotic ground state. For the three remaining sequences (Be, B, C), the PT model produces corrections to the semi-empirical configurations[1]. These corrections, dramatically alter correlation properties such as relative electron positions[3], providing insight into chemical bond angles. They also have a theoretical impact, e.g. they show that for fixed N, and large Z, the order of the Hartree-Fock error is not universal:

$$E_{\mathrm{QM}} - E_{\mathrm{HF}} \begin{cases} = \mathcal{O}(1) & \text{for H, He, Li, N, O, F, Ne} \\ \sim Z & \text{for Be, B C} \end{cases}$$

In this sense, the high-Z limit detects static correlations.

Unfortunately, for atoms with $Z = N$, the energies produced by this model are not chemically accurate. This is a result of its failure to satisfy the virial theorem, which enforces a ratio of the kinetic and potential energies. We therefore extend the model by introducing three variational parameters (analogous to widely-used 'screening parameters'), producing the first mathematical definition of a Configuration Interaction model[2]. This model is 'minimal' in the sense that it contains the smallest basis, with the fewest parameters, such that it is symmetry preserving, asymptotically exact, and satisfies the virial theorem. Up to minimization over the three parameters, it remains exactly soluble by hand. The energies obtained for atoms are comparable to (and in some cases better than) those of much larger numerical models[2].

Some interesting open problems include extension to more electrons[5, 6], inclusion of relativistic effects[7] and use of the simple wave functions to predict molecular geometries[4]. It is possible that these techniques can be extended to molecules, and also that other heuristic explanations of chemical effects may be more rigorously explained by similar methods.

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Electronic Structure of 3d Transition Metal Atoms

Christian B. Mendl

(joint work with Gero Friesecke)

The search for accurate computational methods for the N-electron Schrödinger equation at moderate computational cost has been a focus of activity for several decades. The present talk is a contribution to one part of the picture, wavefunction methods for atoms. We present an algorithmic framework for transition metal atoms which renders asymptotics-based configuration-interaction (CI) computations for atoms with basis sets of up to 50 one-electron spin orbitals, up to 30 electrons, and full resolution of all valence electron correlations feasible.

These asymptotics-based CI methods [1, 2] reproduce, at fixed finite subspace dimension, the exact Schrödinger eigenstates in the limit of fixed electron number N and large nuclear charge Z.

Starting from first principles, the N-electron Schrödinger equation reads

$$(1) \qquad H\psi = E\psi, \quad \psi \in L_a^2\left(\left(\mathbb{R}^3 \times \mathbb{Z}_2\right)^N\right)$$

where H is the Hamiltonian of the system, ψ the wavefunction and E the energy. In our framework, the (non-relativistic, Born-Oppenheimer) Hamiltonian governing atoms/ions with N electrons and nuclear charge Z equals (in atomic units)

$$H = \sum_{i=1}^{N}\left(-\frac{1}{2}\Delta_{\boldsymbol{x}_i} - \frac{Z}{|\boldsymbol{x}_i|}\right) + \sum_{1 \le i < j \le N}\frac{1}{|\boldsymbol{x}_i - \boldsymbol{x}_j|}.$$

It has the well-known symmetry group

$$(2) \qquad SU(2) \times SO(3) \times \mathbb{Z}_2,$$

consisting of simultaneous rotation of electron spins, and simultaneous rotation and sign reversal of electron positions. This leads to the conservation law that the Hamiltonian leaves the simultaneous eigenspaces of the (N-particle) spin, angular momentum and parity operators

$$(3) \qquad \boldsymbol{L}^2,\ L_z,\ \boldsymbol{S}^2,\ S_z,\ \hat{R}$$

invariant.

Our principal contribution is the development of an efficient algorithm that minimizes the curse of dimension. The main savings come from exact (i.e. symbolic) and efficiently automated exploitation of symmetry (2) to perform dimension reduction.

CI methods approximate the electronic Schrödinger equation (1) by projecting it onto a well chosen subspace V:

$$PHP\psi = E\psi, \quad \psi \in V \subset L_a^2\left(\left(\mathbb{R}^3 \times \mathbb{Z}_2\right)^N\right)$$

$$P = \text{ orthogonal projector onto } V,$$

where V is a span of a finite number of Slater determinants $|\chi_{i_1} \cdots \chi_{i_N}\rangle$ built from a finite number of spin orbitals $\{\chi_1, \ldots, \chi_K\} \subset L^2(\mathbb{R}^3 \times \mathbb{Z}_2)$.

We obtain the Ansatz space V via perturbation theory in $1/Z$ [1, 2]. Thus, V contains exact large-Z limits of low eigenstates and resolves gaps and wavefunctions correctly in the large-Z limit, at fixed finite model dimension. E.g., for the carbon atom,

$$V = \text{configurations}\left\{[\text{He}]2s^j\,2p^k \quad \text{such that} \quad j + k = 4\right\}.$$

This corresponds to *FCI in an active space* for the valence electrons. Importantly, we retain the LS symmetries (2) of the atomic Schrödinger equation.

To obtain the symmetry subspaces, we have developed a fast algorithm for diagonalizing the LS operators (3). In detail, we make use of the subshell tensor product structure (such that no explicit antisymmetrization between subshells is needed). Thus, we can iteratively employ *Clebsch-Gordan* formulae. A key point

	sym	conf.	dim	E_{calc} [a.u.]	E_{exp} [a.u.]
Ca	^3D	$4s^1$	2	-674.1634	
	^{1}S	$4s^2$	1	*-674.2442*	-680.1920
Sc	^4F	$4s^1$	3	-756.9381	
	^{2}D	$4s^2$	2	*-756.9968*	-763.8673
Ti	^5F	$4s^1$	8	-845.3714	
	^{3}F	$4s^2$	3	*-845.4210*	-853.3503
V	^6D	$4s^1$	17	-939.5952	
	^{4}F	$4s^2$	8	*-939.6375*	-948.8394
Cr	**^{7}S**	$4s^1$	14	*-1039.7864*	-1050.4914
	^5D	$4s^2$	17	-1039.7852	

TABLE 1. Asymptotics-based CI results with active space $[\text{Ar}]\,3d^j4s^14p^k4d^\ell$ and $[\text{Ar}]\,3d^j4s^24p^k4d^\ell$, respectively. Boldface denotes the experimental ground state symmetry, and italic font the lower of each pair of calculated energies, in exact agreement with the experimental data. Fourth column: Dimension of the symmetry subspace containing the ground state.

of this approach is the fact that the computing time is linear in the number of subshells at fixed angular momentum cutoff, e.g., $1s, 2s, \ldots, ns \sim \mathcal{O}(n)$. Our implementation [4] encodes Slater determinants as binary bitfields. Thus, we can use (typically very fast) bit operations for the necessary calculations.

Finally, we optimize the orbital exponents (so-called "dilation parameters") to minimize the energy *after* symmetry subspace decomposition, which is different from using Hartree-Fock orbitals in CI methods. As added benefit, our solutions satisfy the Virial theorem.

Applications to $3d$ transition metal atoms [3] are in good agreement with experimental data (the results of our computations are shown in table 1). In particular, we reproduce the anomalous magnetic moment and orbital filling of Chromium in the otherwise regular series Ca, Sc, Ti, V, Cr.

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Stochastic Coupled Cluster Theory

ALEXANDER JAMES WILLIAM THOM
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Key to the success of Monte Carlo techniques is the ability to reduce computational effort by converting sums and integrals over extremely large spaces into a series of discrete samples which approximate the full calculation to arbitrary accuracy with increasing numbers of samples. In this talk we cast the Coupled Cluster equations in such a form as can be sampled with Monte Carlo techniques, and show how by parametrization as discrete objects in excitation space the Coupled Cluster equations may be easily approximated and solved[1].

The space in which we shall represent single reference Coupled Cluster theory is that of *excitors* which act with respect to a *reference* Slater determinant. Given an orthonormal set of $2M$ spin-orbitals, we partition them into a set of N which are occupied in the reference determinant, denoted $\phi_i, \phi_j, \ldots \phi_n$, and $2M - N$ unoccupied, or virtual orbitals, denoted $\phi_a, \phi_b, \ldots \phi_f$. The complete space of N-electron Slater determinants in this basis has size $\binom{2M}{N}$ and will be denoted by $D_{\mathbf{m}}$ where $\mathbf{m}$ is an N-vector listing the orbitals occupied in a given determinant. Given the occupied/virtual partitioning, we may also represent all possible determinants

with respect the the reference (which we will denote D_0) by listing the occupied orbitals removed and virtual orbitals added to the determinant, such that D_{ij}^{ab} represents the determinant where i and j in the reference have been replaced by a and b. Further we shall denote by $\hat{a}_{ij}^{ab}$ the *excitation operator* or *excitor* which performs this process, $D_{ij}^{ab} = \hat{a}_{ij}^{ab} D_0$. The excitors behave such that it is not possible to excite from or to an orbital multiple times, e.g. $\hat{a}_i^a \hat{a}_i^b = 0$ and $\hat{a}_i^a \hat{a}_j^a = 0$. By applying each of the $\binom{2M}{N}$ possible excitors to the reference determinant, the whole of of determinant space may be generated, and there is a one-to-one correspondence between excitors and determinants, and so we may denote the excitors by the determinant they would create, $D_{\mathbf{i}} = \hat{a}_{\mathbf{i}} D_0$.

Using these excitors, we may parametrize all possible N-particle wavefunctions in this basis in a number of ways. Coupled Cluster theory uses an exponential *Ansatz* for the wavefunction, $\Psi_{\mathrm{CC}} = e^{\hat{T}} D_0$, where we define $\hat{T} = \sum_{\mathbf{i}} t_{\mathbf{i}} \hat{a}_{\mathbf{i}}$. This seemingly complicated parametrization is used owing to its desirable property of remaining size-consistent even if the sum of excitors is restricted to a limited level of excitation. In essence this is due to the fact that despite a truncation, the exponential ensures that the wavefunction can contain contributions from determinants at all excitation levels.

To determine the parameters $\{t_{\mathbf{i}}\}$, the projected Schrödinger equation is solved; i.e. for all $\mathbf{m}$, we solve

$$(1) \qquad \langle D_{\mathbf{m}} | \hat{H} - E | \Psi_{\mathrm{CC}} \rangle = 0.$$

In general this may be expressed in an iterative form, beginning with a guess for all $\{t_{\mathbf{i}}\}$ and E, and iterating until convergence. The complexity in this arises from the expansion of the exponential

$$(2) \qquad e^{\hat{T}} D_0 = \left[1 + \sum_{\mathbf{i}} t_{\mathbf{i}} \hat{a}_{\mathbf{i}} + \frac{1}{2} \sum_{\mathbf{ij}} t_{\mathbf{i}} t_{\mathbf{j}} \hat{a}_{\mathbf{i}} \hat{a}_{\mathbf{j}} + \frac{1}{3!} \sum_{\mathbf{ijk}} t_{\mathbf{i}} t_{\mathbf{j}} t_{\mathbf{k}} \hat{a}_{\mathbf{i}} \hat{a}_{\mathbf{j}} \hat{a}_{\mathbf{k}} + \dots \right] D_0.$$

Instead of explicitly rearranging the equations (1) in an iterative form, which is the means by which many conventional implementations work, we note that solutions to the Coupled Cluster equations must also satisfy

$$(3) \qquad \langle D_{\mathbf{m}} | 1 - \delta\tau (\hat{H} - E) | \Psi_{\mathrm{CC}} \rangle = \langle D_{\mathbf{m}} | \Psi_{\mathrm{CC}} \rangle,$$

where $\delta\tau$ is some small positive number We may write this as an iteration from time τ to $\tau + \delta\tau$,

$$(4) \qquad t_{\mathbf{m}}(\tau) - \delta\tau \langle D_{\mathbf{m}} | \hat{H} - E | \Psi_{\mathrm{CC}}(\tau) \rangle = t_{\mathbf{m}}(\tau + \delta\tau).$$

Iterating in this form will result in a solution to the Coupled Cluster equations, though the evaluation of the second term in (4) is not trivial. Indeed, it turns out to be easier to sample this term and additionally to *discretize* the amplitudes, as has been done in the FCIQMC method[2, 3]. In analogy to Anderson[5], we shall represent amplitudes of excitors by sets of *excitor particles* or *excips*. Each excip sits on a given excitor, $\hat{a}_{\mathbf{n}}$ and is given a positive or negative sign. The mean signed number of excips at a given excitor will be taken to represent its (unnormalized)

amplitude. We may approximate the action of (4), with some simple stochastic steps.

The first is sampling Ψ_{CC}, by selecting randomly from all possible clusters in (2), e.g. $t_{\mathbf{i}}t_{\mathbf{j}}\hat{a}_{\mathbf{i}}\hat{a}_{\mathbf{j}}D_0$. Once selected the cluster is collapsed to form determinant, $t_{\mathbf{i}}t_{\mathbf{j}}\hat{a}_{\mathbf{i}}\hat{a}_{\mathbf{j}}D_0 = t_{\mathbf{i}}t_{\mathbf{j}}\hat{a}_{\mathbf{n}}D_0 = t_{\mathbf{i}}t_{\mathbf{j}}D_{\mathbf{n}}$. This process may involve some sign changes or even result in zero (if $\mathbf{i}$ and $\mathbf{j}$ excite from the same occupied or to the same virtual orbitals).

The second stochastic process is the sampling the action of the Hamiltonian. For each $D_{\mathbf{n}}$ generated from sampling Ψ_{CC}, we *could* enumerate all possible $D_{\mathbf{m}}$, evaluating $\langle D_{\mathbf{m}}|\hat{H} - E|D_{\mathbf{n}}\rangle$ and updating $t_{\mathbf{m}}$ accordingly. As the Hamiltonian only connects up to single and double excitations from a determinant, we may instead sample this process by randomly picking $D_{\mathbf{m}}$ as a single or double excitation of $D_{\mathbf{n}}$, and updating $t_{\mathbf{m}}$ appropriately. We may instead sample this by selecting a single connected determinant and creating an appropriately signed excip there with a probability proportional to $|\delta\tau H_{\mathbf{mn}}|$. Additionally, as the diagonal elements of the Hamiltonian are large, we explicitly perform the case when $\mathbf{m} = \mathbf{n}$, this time with probability proportional to $|\delta\tau(H_{\mathbf{nn}} - E)|$.

Finally, after these two processes have been done for as many clusters as required to be sampled, the new list of excips is sorted and any opposite signed pairs of excips on the same excitor removed.

We additionally show how, with the application of the initiator approximation of Cleland and Alavi[4], this method can vastly reduce the storage and requirements for Coupled Cluster calculations. We present results of CCSDTQ calculations on the neon atom with basis sets up to cc-pV6Z and demonstrate calculations beyond the capability of other present methods.

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Relativistic effects in highly charged ions

ROBERT LANG

(joint work with Gero Friesecke)

We study relativistic effects in highly charged ions via perturbation theory. Our starting point is the non-relativistic Schrödinger operator,

$$(1) \quad H(N) := H_0(N) + V_{\mathrm{ee}}(N) := \sum_{i=1}^{N} \left(-\frac{1}{2}\Delta_i - \frac{Z}{|x_i|} \right) + \frac{1}{2}\sum_{i \neq j} \frac{1}{|x_i - x_j|} \ ,$$

decomposed into a non-interacting part, $H_0(N)$, which contains only kinetic terms and the electron-nucleus interactions, and a part describing the electron-electron interaction, $V_{\mathrm{ee}}(N)$. Such N-electron systems can be treated perturbatively in the iso-electronic limit (fixed N, but $Z \to \infty$) due to a rescaling of the eigenfunction $\psi(x, s)$ of $H(N)$:

$$(2) \quad \widetilde{\psi}(x_i, s_i) := Z^{-3N/2}\,\psi(x_i/Z, s_i), \quad i = 1, \ldots, N \ ,$$

where x_i and s_i denote, respectively, the spatial and spin coordinate of the i-th electron. This leads to the eigenvalue equation

$$(3) \quad \left(H_0(N) + \frac{1}{Z}V_{\mathrm{ee}}(N) \right) \widetilde{\psi} = \frac{E}{Z^2}\widetilde{\psi} \ ,$$

where the interacting part becomes negligible for $Z \to \infty$.

Let P denote the orthogonal projection onto the non-interacting ground state $V_0(N)$. In [1, 2] the eigenvalue equation $PH(N)P\psi = E\psi$ is solved analytically for $\psi \in V_0(N)$ with $3 \leq N \leq 10$. More precisely, the eigenstates of this so-called perturbation-theory (PT) model are the exact eigenstates of $H(N)$ for $Z \to \infty$. Inspecting the spectral gaps predicted by the PT model and comparing them to experimental data from the NIST database [6] shows that for too large values of Z the non-relativistic PT model cannot describe nature accurately and relativistic effects become important.

The relativistic corrections to the spectra are implemented by switching from Schrödinger theory to Dirac theory, which models relativistic one-fermion systems. We assume that the relativistic corrections can be written as one-particle operators

$$(4) \quad H^{\mathrm{X}}(N) := \sum_{i=1}^{N} \delta^{\mathrm{X}}(i), \quad \mathrm{X} \in \{\mathrm{D, P, LS}\} \ ,$$

with the well-known corrections [3]: Darwin term, $\delta^{\mathrm{D}} = \pi Z\,\delta^{(3)}/2$, the next-to-leading-order term of the energy-momentum relation, $\delta^{\mathrm{P}} = -p^4/8$, and the LS-coupling, $\delta^{\mathrm{LS}} = Z/2\,(L \cdot S)/|x|^3$. From this we define the relativistic Hamiltonian,

$$(5) \quad H_{\mathrm{rel}}(N) := H(N) + \frac{1}{c_0^2}\left[H^{\mathrm{D}}(N) + H^{\mathrm{P}}(N) + H^{\mathrm{LS}}(N) \right] \ .$$

The speed of light reads in atomic units $c_0 = 1/\alpha \approx 137$, with α being the fine-structure constant.

At first order perturbation theory only the eigenvalues are corrected the eigenstates remain the same:

$$(6) \qquad E = -|A|Z^2 + BZ + \frac{C}{c_0^2}Z^4 \, ,$$

where $A = A(N) \in \mathbb{Q}^-$ describes the electron-nucleus interactions, $B = B(N) \in \mathbb{R}$ takes into account the electron-electron interactions, and $C = C^J(N) \in \mathbb{Q}$ incorporates the relativistic corrections. For very large values of Z the last term becomes dominant, but for $Z \lesssim 40$ the applicability of our perturbative ansatz holds because of the prefactor $1/c_0^2$. For instance, for Lithium [1, 4] one has for the ground state ($L = 0, S = 1/2 \Rightarrow J = 1/2$), and its first excited state ($L = 1, S = 1/2 \Rightarrow J = 1/2, 3/2$):

$$(7) \qquad A_{\mathrm{GS}} = -\frac{9}{8} \, , \quad B_{\mathrm{GS}} = \frac{5965}{5832} \, , \quad C_{\mathrm{GS}}^{1/2} = -\frac{37}{128} \, ,$$

$$(8) \qquad A_{\mathrm{E1}} = -\frac{9}{8} \, , \quad B_{\mathrm{E1}} = \frac{57397}{52488} \, , \quad C_{\mathrm{E1}}^{1/2} = -\frac{37}{128} \, , \quad C_{\mathrm{E1}}^{3/2} = -\frac{33}{128} \, .$$

Note, that the relativistic corrections for the ground state and the first-excited state with total angular momentum $J = 1/2$ coincide, $C_{\mathrm{GS}}^{1/2} = C_{\mathrm{E1}}^{1/2} = -37/128$, although all contributions to them differ. Therefore, the spectral gap between these two states should not experience a relativistic correction; indeed, the NIST data confirm this prediction as it is shown in the left figure below.

So far we have reached a qualitative description of relativistic corrections. The quantitative agreement in the left figure between theory (red line) and experiment (circles) can be improved by using the Rayleigh-Ritz variational principle as described in [5]: the effective nuclear charge, $Z_{\mathrm{eff}} := Z - \Delta(Z) < Z$, incorporates shielding effects for the outermost electron induced by the closed first shell.

$$(9) \qquad \langle \psi_{\mathrm{E1}} | H(N = 3) | \psi_{\mathrm{E1}} \rangle \stackrel{!}{=} \min \quad \Rightarrow \quad \Delta(Z) \, ,$$
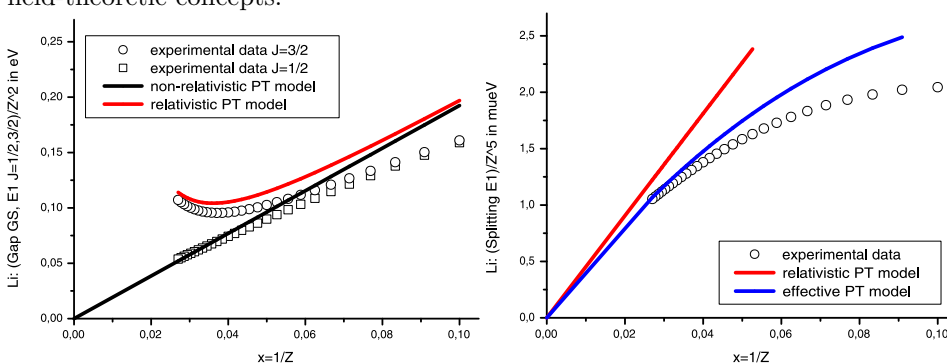
for instance $\Delta(3) = 1.9542 \, , \ \Delta(10) = 1.7082 \, , \ \Delta(30) = 1.6457$. Note, that the shielding is quenched for increasing Z which agrees with the fact that effects based on electron-electron interactions become negligible for $Z \to \infty$. We test the prediction of the relativistic PT model by inspecting the fine structure (of Lithium), which is a purely relativistic effect and is not described by $H(N)$ at all. Before, the spectral gaps have been rescaled by Z^2 leading to a straight line in $1/Z$. Now, for the splitting we rescale by Z^5 which leads in the case of vanishing shielding effects to a straight line in $1/Z$:

$$(10) \qquad \frac{C_{\mathrm{E1}}^{3/2} - C_{\mathrm{E1}}^{1/2}}{Z^5} = \frac{1}{32} \frac{1}{Z} \left(1 - \frac{\Delta(Z)}{Z} \right)^3 \, .$$

The comparision to the NIST database is shown in the right figure below: the relativistic PT model with effective nuclear charge agrees very well with the available experimental data points for Z being large enough.

In summary, highly charged ions provide an elegant setting to study relativistic effects and explore them qualitatively by first-order parturbation theory. The

applicability of the relativistic PT model is limited to cases where the relativistic term in (6) is sub-dominant. In the ultra-relativistic case one has to incorporate field-theoretic concepts.

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Using sparse grids to solve the vibrational Schrödinger equation

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(joint work with Gustavo Avila)

A new method is presented for solving the vibrational Schrödinger equation

$$H\psi_n = E_n\psi_n$$

where

$$H = T + V$$

with T a kinetic energy operator (KEO) and V a (Born-Oppenheimer) potential. The vibrational KEO may be very complicated but the potential is smooth (at least where wavefunctions have non-negligible amplitude). To compute vibrational energy levels and wavefunctions one must deal with $3N - 6$ coordinates, where N is the number of atoms.

The most straightforward approach for solving the Schrödinger equation (Galerkin) requires representing wavefunctions with basis functions

$$\psi_k(\boldsymbol{q}) = \sum_n c_n^k$$

evaluating Hamiltonian matrix elements (integrals), and computing eigenvalues and eigenvectors of the Hamiltonian matrix. Typically one requires at least hundreds of eigenvalues (and eigenvectors). [1, 2]

For the $J = 0$ problem, the most obvious basis functions are product functions:

$$f_{n_1,n_2,\cdots} = \phi_{n_1}(r_1)\phi_{n_2}(r_2)\cdots\phi_{n_D}(r_D)\cdots$$

Between 10 and 100 1-d functions are required for each coordinate and therefore the total basis (matrix) size is $\sim 10^{3N-6}$. To compute eigenvalues of a matrix this large we use an iterative eigensolver – the Lanczos algorithm and this requires evaluating matrix-vector products.

When the Hamiltonian matrix is a sum of terms each of which is of the form

$$A_{n1'n1} \ B_{n2'n2} \ C_{n3'n3} \ \cdots$$

then matrix-vector products can be evaluated at a cost that scales as n^{D+1}, where n is a representative number of univariate functions, and D is the number of coordinates. Hamiltonian matrix-vector products can then be evaluated term by term. Note that the n^{D+1} scaling is independent of the sparsity of the matrix.[3] For each term, matrix-vector products are evaluated by moving sums to the right:

$$= \sum_{n1n2n3} A_{n1'n1} \ B_{n2'n2} \ C_{n3'n3} \ v_{n1n2n3}$$

$$= \sum_{n1} A_{n1'n1} \sum_{n2} B_{n2'n2} \sum_{n3} C_{n3'n3} v_{n1n2n3}$$

Although the KEO is usually in this sum of products form, the potential is in general a complex function. One option is to approximate the potential as a sum of products using tensor or neural network methods. [6, 5] Another is to use the original potential and quadrature. Surprisingly, multidimensional quadrature does not significantly increase the cost of the matrix-vector products. With a product basis and a product quadrature grid the cost of matrix-vector products still scales as n^{D+1}. To illustrate the idea consider a two dimensional example. The desired matrix-vector product is,

$$w_{l'm'} = \sum_{lm} V_{l'm',lm} \ x_{lm} \ .$$

The potential matrix elements

$$V_{l'm',lm} = \int d\theta \int d\phi F_{l'}(\theta)G_{m'}(\phi)V(\theta,\phi)G_m(\phi)F_l(\theta)$$

are replaced by a quadrature approximation

$$V_{l'm',lm} \approx \sum_{\beta\gamma} T_{l'\beta} \, Q_{m'\gamma} \, V(\theta_\beta, \phi_\gamma) \, Q_{m\gamma} \, T_{l\beta}$$

with

$$T_{l\beta} \sim F_l(\theta_\beta) \; , \; Q_{m\gamma} \sim G_m(\phi_\gamma) \; .$$

and the required matrix-vector product becomes,

$$w_{l'm'} = \sum_{lm} \sum_{\beta\gamma} T_{l'\beta} \, Q_{m'\gamma} \, V(\theta_\beta, \phi_\gamma) \, Q_{m\gamma} \, T_{l\beta} \, x_{lm} \; .$$

It can be evaluated by doing sums sequentially,

$$w_{l'm'} = \sum_{\beta} T_{l'\beta} \sum_{\gamma} Q_{m'\gamma} \, V(\theta_\beta, \phi_\gamma) \sum_{m} Q_{m\gamma} \sum_{l} T_{l\beta} \, x_{lm}$$

at a cost that scales as n^{D+1}.

Although the CPU cost is moderate the memory cost is a problem. We must store vectors labeled by basis indices, vectors labeled by grid indices, and vectors labeled by some basis indices and some grid indices. Owing to the fact that, for a given coordinate, one typically needs more quadrature points than basis functions, the largest vectors are those labeled by grid indices.

The size of the basis-labeled vectors can be reduced by pruning the basis. The product basis functions are usually eigenfunctions of a zeroth-order Hamiltonian, H_0 that is a sum of 1d Hamiltonians (separable) pieces,

$$H = H_0 + \Delta$$

If all the pieces are identical, removing basis functions with large zeroth-order energies means discarding basis functions for which

$$\sum_c n_c > b \; .$$

The basis size reduction obtained in this fashion is significant. For example, if $3N - 6 = 15$ and 15 basis functions are used for each coordinate then the size of the direct product basis is 4×10^{17}, but the size of the basis pruned by discarding all functions for which $\sum_c n_c > b = 15$ is reduced to 7.7×10^7. Pruning the basis not only reduces the size of vectors, it also decreases the number of required Lanczos iterations. An useful pruning scheme allows one to evaluate matrix-vector products efficiently by doing sums sequentially. [4]

When a basis is pruned by retaining functions (in three dimensions) with $n_1 + n_2 + n_3 \leq b$ then $n_1^{max} = b - n_2 - n_3$ and $n_2^{max} = b - n_3$. Therefore, with this pruning scheme it is possible to evaluate sums sequentially because

$$\sum_{n_3}^{b} \sum_{n_2}^{n_2^{max}(n3)} \sum_{n_1}^{n_1^{max}(n3,n2)} A_{n_1 n_1} B_{n_2 n_2} C_{n_3 n_3} \, v_{n1n2n3}$$

can be replaced by

$$\sum_{n_3}^{b} C_{n_3 n_3} \sum_{n_2}^{n_2^{max}(n3)} B_{n_2 n_2} \sum_{n_1}^{n_1^{max}(n3,n2)} A_{n_1 n_1}\, v_{n1n2n3}$$

Although it is possible to prune the basis without jeopardizing the efficiency of matrix-vector products the size of the quadrature grid remains a problem. When a product (e.g. Gauss) grid is used the matrix-vector product is:

$$v2(n_3', n_2', n_1') = \sum_{k_1=1}^{k_1^{max}} T_{n_1' k_1} \sum_{k_2=1}^{k_2^{max}} T_{n_2' k_2} \sum_{k_3=1}^{k_3^{max}} T_{n_3' k_3}$$
$$V(q_1^{k_1}, q_2^{k_2}, q_3^{k_3})$$
$$\sum_{n_3=0}^{n_3^{max}} T_{n_3 k_3} \sum_{n_2=0}^{n_2^{max}} T_{n_2 k_2} \sum_{n_1=0}^{n_1^{max}} T_{n_1 k_1}\, v1(n_3, n_2, n_1)$$

The largest vectors have as many elements as there are quadrature points $\sim n^D$. It is the size of the quadrature grid that prevents one from solving more difficult problems. To overcome this limitation one must find a smaller quadrature grid with which all matrix elements are nevertheless accurately computed and also ensure that the smaller grid has enough structure that it is possible to efficiently evaluate matrix-vector products.

Instead of a product grid we use a Smolyak grid. [7, 8, 9] The Smolyak quadrature equation [10] for integrating a function can be written as a sum of D-dimensional product quadrature grids,

$$S(D, K) = \sum_{f(\boldsymbol{i}) \leq H} C_{i_1, \dots, i_D}[Q^{i_1}(x_1) \otimes \cdots \otimes Q^{i_D}(x_D)],$$

A Smolyak quadrature built from nested 1D quadratures is advantageous because the total number of points is smaller and because it has the structure required to make efficient matrix-vector products possible. We use nested 1D quadratures constructed for our basis which is composed of products of 1D factors

$$\Phi_{n_1\cdots, n_{12}}(q_1, \cdots, q_{12}) = \chi_{n_1}(q_1) \cdots \chi_{n_{12}}(q_{12}),$$
$$n_c = 0, \cdots, n_{max}^c, \text{ for } c = 1, \cdots, 12$$

with

$$\chi_n(q) = A_n H_n(q)\exp(\frac{-q^2}{2}).$$

To build the nested quadratures we use ideas related to those of Patterson. For C_2H_4 we use

$$N_i = 1, 3, 3, 7, 9, 9, 9, 9, 17, 19, 19, 19, 31, 33, 41, 41, \cdots$$
$$d_i = 1, 5, 5, 7, 15, 15, 15, 15, 17, 29, 29, 29, 31, 33, 61, 61, \cdots,$$

where N_i is the number of points in quadrature Q^i and d_i is the maximum degree exactly integrated by quadrature Q^i. Note that we have not chosen the quadratures to minimise the number of points required to evaluate *all* monomials

of degree $2K - 1$. Instead, we have chosen to increase the number of important monomials, with a subset of the coordinates, for which integrals are exact.

In our calculations we use a KEO in normal coordinates,

$$\hat{T} = -\frac{1}{2} \sum_k^D \omega_k \frac{\partial^2}{\partial q_k{}^2} + K \ .$$

K is a complicated term whose treatment is presented in reference [9]. The Lanczos algorithm is used, without re-orthogonalisation, to compute eigenvalues and eigenvectors.

The hardest part of the calculation is the potential matrix-vector product. A Smolyak grid has fewer points, but the Smolyak quadrature equation (Eq. (1)) has a sum over contributing grids (the sum over $f(i) \leq H$ in Eq. (1)). To reduce the cost of the potential matrix-vector product it is crucial to avoid repeating this sum at each Lanczos iteration. This can be done by incorporating the sum over contributions into weights. The Smolyak quadrature of a function f can be written,

$$
\begin{aligned}
&S(6, K) f(q_1, q_2, q_3, q_4, q_5, q_6) \\
&= \sum_{k_1}^{N_1} \sum_{k_2}^{N_2} \sum_{k_3}^{N_3} \sum_{k_4}^{N_4} \sum_{k_5}^{N_5} \sum_{k_6}^{N_6} w(k_6, k_5, k_4, k_3, k_2, k_1) \\
&\qquad \times f(q_1^{k_1}, q_2^{k_2}, q_3^{k_3}, q_4^{k_4}, q_5^{k_5}, q_6^{k_6})
\end{aligned} \qquad ,
$$

where k_c labels a quadrature point for coordinate c and N_c is the maximum number of points for coordinate q_c. N_1 is independent of $k_{c \neq 1}$

$$N_1 = N\left((H - (D-1))\right)$$

Using the notation $N_j = N(j)$ the other maxima are

$$N_c \quad = \quad N\left(H - \sum_{i=1}^{c-1} g(k_i) - (D - c)\right)$$

where $c = 2, 3, \cdots$, and $g(k)$ is the smallest quadrature rule in the sequence of quadratures that contains point k.

The new weights are,

$$w(k_6, \cdots, k_1) = \sum_{f(\mathbf{i}) \leq H} C_{i_1, \cdots, i_6} \, {}^{i_1}w_{k_1} \cdots {}^{i_D}w_{k_6},$$

where ${}^{i_c}w_{k_c}$ is the (1D) weight for the point $q_c^{k_c} \in Q^{i_c}$, and ${}^i w_k = 0$ if $q^k \notin Q^i$. In terms of these weights the potential matrix-vector product is computed by doing sums sequentially,

$$
\begin{aligned}
v2(n_3', n_2', n_1') &= \sum_{k_1=1}^{N_1} T_{n_1' k_1} \sum_{k_2=1}^{N_2} T_{n_2' k_2} \sum_{k_3=1}^{N_3} T_{n_3' k_3} \\
&\qquad w(k_3, k_2, k_1) V(q_1^{k_1}, q_2^{k_2}, q_3^{k_3}) \\
&\sum_{n_3=0}^{n_3^{\max}} T_{n_3 k_3} \sum_{n_2=0}^{n_2^{\max}} T_{n_2 k_2} \sum_{n_1=0}^{n_1^{\max}} T_{n_1 k_1} \\
&\qquad v1(n_3, n_2, n_1) \ ,
\end{aligned}
$$

where $T_{nk} = A_n H_n(q_k)$. Note that by defining new weights that combine the Smolyak coefficients $C_{i_1, \cdots, i_6}$ and the $^{i_c}w_{k_c}$ we avoid the need to sum over contributing grids at each Lanczos iteration. [7, 8, 9]

In Ref. [9] we present vibrational energy levels of C_2H_4 computed with a basis whose size is determined by $n_1 + \cdots + n_{12} \leq 11$. There are 1.4×10^6 basis functions. A Smolyak grid with $H = 25$ with 1.5×10^8 quadrature points was used. A product Gauss grid with comparable accuracy has $\sim 6 \times 10^{13}$ points

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Unique Hartree-Fock Minimizers for Closed Shell Atoms

FABIAN HANTSCH

(joint work with Marcel Griesemer)

In this talk we discussed the problem of uniqueness of minimizers for the Hartree-Fock functional of atoms. It was shown that the Hartree-Fock ground state is unique provided the number of electrons is of the form $N = 2\sum_{n=1}^{s} n^2$, $s \in \mathbb{N}$, and the atomic number Z is sufficiently large compared to N. More specifically, a two-electron atom with atomic number $Z \geq 35$ has a unique Hartree-Fock ground state given by two orbitals with opposite spins and identical spatial wave functions. Our result implies that the General, Unrestricted and Restricted Hartree-Fock (GHF, UHF, RHF) ground states coincide. The fact that this is wrong for $N = 2$ and some $Z > 1$ [2] shows the necessity of some lower bound on Z for the uniqueness

of the ground state. Our method also applies to Restricted Hartree-Fock theory where we can allow for any atom whose electrons are in an arbitrary closed shell configuration. We refer to [1] for further details and more results on existence and uniqueness of critical points for both the Hartree-Fock and the Hartree functionals.

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QC-DMRG and recent advances in tensor product approximation

REINHOLD SCHNEIDER

The DMRG algorithm is a well established tool for computing strongly correlated quantum systems, widely used for lattice spin systems [S]. Presently we consider its application to the numerical solution of the electronic Schrödinger equation the QC-DMRG (quantum chemistry DMRG) e.g. [LH]. The numerical solution of partial differential equations in d dimensions, $d >> 1$, is hardly hempered by the unfavourable scaling $\mathcal{O}(n^d)$ of traditional approximation methods, often refered to as the *curse of dimensionality*. Approximation by a sum of tensor products of single variate functions offer an efficient and very flexible tool for data sparse approximation for high dimensional tensors or high dimensional functions. For convenience of exposition, we will consider a tensor $U \in \mathbb{R}^{n_1 \times \dots \times n_d}$ of order (or dimension), as a multivariate function or multi-indexed array, of the form

$$\underline{x} \mapsto U(\underline{x}) \;=\; U(x_1, \dots, x_d) \;:\; \mathcal{I}_1 \times \dots \times \mathcal{I}_d \;\longrightarrow\; \mathbb{K} \;,\; \mathbb{K} = \mathbb{R} \text{ or } \mathbb{C}$$

with variables or indices x_i from finite index sets $\mathcal{I}_i := \{1, \dots, n_i\}$, $i \in \{1, \dots, d\}$, where $d \in \mathbb{N}$ and $n_1, \dots, n_d$. Unfortunately, except the elementary (matrix) case $d = 2$, the *canonical format*

$$U(x_1, \dots, x_d) = \sum_{i=1}^{r_c} U_i = \sum_{i=1}^{r_c} \bigotimes_{\nu=1}^{d} u_{i,\nu}(x_\nu) = \sum_{i=1}^{r_c} \bigotimes_{\nu=1}^{d} u_\nu(x_\nu, i) \;,$$

suffers from various shortcomings, making the actual computation of a low-rank approximation a numerically hazardous task. Nevertheless, it reduces the amount of required data to $\mathcal{O}(nr_c d)$. This is in contrast the so-called *Tucker decomposition*, In essence, the Tucker format is a subspace approximation. It provides a kind of parametrization which is appropriate for optimization and the treatment dynamical equations. This concept is well estbalished in phyiscs, e.g the MCSCF and MCTHF methods. It has been shown, that the Tucker format provides an embedded manifold. Since the representation of a tensor in the Tucker format requires $\mathcal{O}(r^d + dn)$, $n := \max\{n_\nu : 1 \leq \nu \leq d\}$, degrees of of freedom (DOF), it does not circumvent from the curse of dimensionality. To overcome this dilemma, new formats built on a hierarchical structure for tensor decomposition has been

introduced in [HT]. and [TT]. Where the latter TT format is a special and simplest case of the more general hierachical Tucker format in [HT]. Although these formats have been apparent in various concepts in quantum mechanics, e.g. like tree tensor networks ($\simeq$ HT) and matrix product states ($\simeq TT$), its perspective from mathematics is independent of its application, focusing on issues like approximation, existence and stability. A representation of a tensor $U \in \mathbb{R}^{n_1 \times \cdots \times n_d}$ in the TT tensor format rewrites an order-d tensor in the form

$$U(\underline{x}) = \sum_{k_1=1}^{r_1} \ldots \sum_{k_{d-1}=1}^{r_{d-1}} U_1(x_1, k_1) U_2(k_1, x_2, k_2) \ldots U_{d-1}(k_{d-2}, x_{d-1}, k_{d-1}) U_d(k_{d-1}, x_d),$$

where for $2 \leq i \leq d-1$, $(k_{i-1}, x_i, k_i) \mapsto U_i(k_{i-1}, x_i, k_i) \in \mathbb{R}^{r_{i-1} \times n_i \times r_i}$. Recently Hackbusch and Falco proved the existence of best approximation, and we have shown that the TT-format provides an embedded manifold, see e.g [HRS-1] for further details. Therefore, the TT format requires only a data complexity of order $\mathcal{O}(nr^2 d)$, but it is inheriting all stability issues of the Tucker format. The *electronic Schrödinger equation*, is the basic equation in quantum chemistry It describes the stationary and non-relativistic behavior of an ensemble of N electron exposed to an electric Coulomb field given by fixed nuclei. The electron wave function Ψ obeys the *Pauli antisymmetry principle* Since the novel tensor formats are sensitive w.r.t. permutation of variables, we pursue an alternativ way [HRS-1], using the discrete Fock space $\mathcal{F}$ built by all Slater determinants

$$\Psi_{SL}[k_1, \ldots, k_N](\mathbf{x}_1, s_1; \ldots; \mathbf{x}_N, s_N) \quad := \quad \frac{1}{\sqrt{N!}} \det(\varphi_{k_i}(\mathbf{x}_j, s_j))_{i,j=1}^N.$$

out of a given orthonormal orbital basis set, $\mathcal{X}_h := \text{span} \{\varphi_i : i = 1, \ldots, d\}$.

$$\mathcal{F} := \bigoplus_{N=1}^d \mathcal{V}_{FCI}^N = \bigoplus_{N=1}^d \bigwedge_{i=1}^N \mathcal{X}_h = \{\Psi : \Psi = \sum_\mu c_\mu \Psi_\mu\} \, .$$

As standard in FCI computation, a labeling of indices $\mu \in \mathcal{I}$ by an binary string of length d

$$\text{e.g.:} \quad \underline{\mu} \quad = \quad (0, 0, 1, 1, 0, \ldots) =: (\mu_1, \ldots, \mu_i, \ldots, \mu_d\} \, , \ \mu_i = 0, 1 \, ,$$

- $\mu_i = 1$ means φ_i is (occupied) in $\Psi[\ldots]$.
- $\mu_i = 0$ means φ_i is absend (not occupied) in $\Psi[\ldots]$.

yields that the discrete Fock space could be completely parametrized by tensors

$$\mathcal{F} \simeq \{\mathbf{c} : \mu \mapsto \mathbf{c}(\mu_0, \ldots, \mu_{d-1}) = c_\mu \, , \ \mu_i = 0, 1 \} = \bigotimes_{i=1}^d \mathbb{K}^2 \, .$$

Instead of bit manipulations we can reformulate the calculus of second quantization with creation and annihilation operators $a_p^{(\dagger)}, a_p$ by simple Kronecker products of the 2×2 matrices

$$A := \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} , \ A^T = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} , \ S := \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} , I := \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} .$$

One obtains that the discrete creation (annihilation) operators corresponds to

$$a_p^{(\dagger)} \simeq \mathbf{A}_p^{(T)} := S \otimes \ldots \otimes S \otimes A_{(p)}^{(T)} \otimes I \otimes \ldots \otimes I$$

where $A_{(p)}$ means that A appears on the p-th position in the product. We adhere completely on the present one-to-one correspondence between the (discrete) Fock space and the tensor space of corresonding amplitudes, to describe the (discrete) Hamiltonian $\mathbf{H} = \sum_{p,q=1}^{d} h_p^q \mathbf{A}_p^T \mathbf{A}_q + \sum_{p,q,r,s=1}^{d} g_{r,s}^{p,q} \mathbf{A}_r^T \mathbf{A}_s^T \mathbf{A}_p \mathbf{A}_q$ and the particle number operator $\mathbf{P} = \sum_{p,q=1}^{d} \mathbf{A}_p^T \mathbf{A}_q$, where h_p^q and $g_{r,s}^{p,q}$ denote the well known one and two electron integrals,

$$h_q^p := \langle \varphi_q, (\frac{-1}{2}\Delta - V_{core})\varphi_p \rangle \ , \ g_{r,s}^{p,q} := \frac{1}{2}\langle \varphi_r(\mathbf{x}, s_1)\varphi_s(\mathbf{y}, s_2), \frac{\varphi_p(\mathbf{x}, s_1)\varphi_q(\mathbf{y}, s_2)}{|\mathbf{x} - \mathbf{y}|} \rangle \ .$$

To obtain the ground state of an N-electron system, we have to take care about required symmetries. We can casted full CI Schrödinger equation into the variational form [HRS-1] So far, except the full CI approximation, no further approximation has been applied. Moreover the above representation depends crucuially on the choice of the underlying basis functions. Due to the combinatorial complexity of FCI computation, further approximations are required. We will focus on tensor product approximation by solving the following variational problem along the manifold of TT tensors (or matrix product states) of prescribed rank

$$\{\mathbf{U} = (U(\underline{\mu})) = \text{argmin}\{\langle \mathbf{HU}, \mathbf{U} \rangle : \langle \mathbf{U}, \mathbf{U} \rangle = 1 \ , \ \mathbf{PU} = N \ , \mathbf{U} \in \mathcal{T}_\mathbf{r} \ \} \ .$$

We remark that the crucial parameter, the rank r_i, $i = 1, \ldots, d-1$, is defined by the rank $r_i = \text{rank}\big[U_{\mu_1,\ldots,\mu_i}^{\mu_{i+1},\ldots,\mu_d}\big]$ of the matricisation or unfolding of the tensor

$$U(\mu_1, \ldots, \mu_i, \mu_{i+1}, \ldots, \mu_d) \simeq U_{\mu_1,\ldots,\mu_i}^{\mu_{i+1},\ldots,\mu_d} \ .$$

Separating the complete system into two subsystems systems A, B, built by the orbital basis sets $\{\varphi_1 \ldots, \varphi_i\}$ and $\{\varphi_{i+1}, \ldots, \varphi_d\}$, the above observation implies that the TT format or MPS describes the interaction between these two systems explicitly. In particular, if both systems are independent, the rank $r_i = 1$, thus providing size consistency. The above variational problem can be tackled algorithmitically by an alternating direction approach an *alternating linear squares scheme* (ALS) . Let us fix all tensors $\mathbf{U}_i(\mu_i)$, $i \in \{1, \ldots, d\}\backslash\{j\}$, except the one for index j. We are going to optimize $U_j(k_{j-1}, x_j, k_j)$ in an micro-iteration step. We perform this procedure sequentially with $j = 1, \ldots, d-1$, then we repeat the relaxation procedure in the opposite direction. This scheme has the disadvantage that the ranks r_j are given a priorily. To adapt the individual ranks r_j, we modify the scheme, by concatenating two variables μ_j, μ_{j+1} into one (μ_j, μ_{j+1}), and searching for an optimized component $W(k_{j-1}, \mu_j, \mu_{j+1}, k_{j+1})$. In a subsequent decimation step, we approximate $\mathbf{W}(\mu_j, \mu_{j+1}) = \mathbf{U}_j(\mu_j)\mathbf{V}_j(\mu_{j+1})$ by low rank, e.g. by means of SVD, up to a tolerance ϵ_j. We keep $\mathbf{U}_j$ and proceed by computing $\mathbf{W}(\mu_{j+1}, \mu_{j+2})$ next. This modified alternating linear scheme (MALS) applied to this problem resembles exactly the DMRG (density matrix renormalization group) method [S] for spin chains.

Summary: The TT format, resp. matrix product states approximates the Full CI solution in a data sparse way. Although it permeates the full CI space, all computations can be performed within polynomial complexity. The electron density as well as reduced one- and two- body density matrices can be computed in polynomial cost. It provides inside in particular separations into subsystems and its entanglement. This make this approach atractive for the computation of stronlgy correlated systems, where Coupled Cluster methods are failing. The approximation depends crucially on the choice of orbital basis functions and its ordering.

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Projected quasiparticle theory for molecular electronic structure

Gustavo E. Scuseria

(joint work with Carlos A. Jimenez-Hoyos, Thomas M. Henderson, Kousik Samanta, Jason K. Ellis)

We derive and implement symmetry-projected Hartree-Fock-Bogoliubov (HFB) equations and apply them to the molecular electronic structure problem. All symmetries (particle number, spin, spatial, and complex conjugation) are deliberately broken and restored in a self-consistent variation-after-projection approach. We show that the resulting method yields a comprehensive black-box treatment of strong correlations with effective one-electron (mean-field) computational cost. The ensuing wave function is of multireference character and permeates the entire Hilbert space of the problem. The energy expression is different from regular HFB theory but remains a functional of an independent quasiparticle density matrix. All reduced density matrices are expressible as an integration of transition density matrices over a gauge grid. We present several proof-of-principle examples demonstrating the compelling power of projected quasiparticle theory for electronic structure theory.

There are many mathematical aspects of this work that I discussed. These include but are not limited to the role of antiunitary symmetries that do not carry

"good" quantum numbers and the importance of coherent states in symmetry breaking and restoration.

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