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Mathematical and Numerical Aspects of Quantum Chemistry Problems

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ABSTRACT. This workshop was aimed at strengthtening the interactions between well established experts in quantum chemistry, mathematical analysis, numerical analysis and computational metodology. Most of the mathematicians present in the worskhop have already contributed to the theoretical and numerical study of models in quantum physics and chemistry. Some others, familiar with contiguous fiels, were new to chemistry. Several distinguished researchers in theoretical chemistry participated in the workshop, and presented the mathematical and computational challenges of the field.

Introduction by the Organisers

Computational quantum chemistry is nowadays a very lively topic, which has a huge number of applications ranging from Chemistry itself to biology and materials science. Most of the models are written in terms of variational problems involving partial differential equations. Mathematics can play an important role in the analysis of those models as well as in their numerical analysis and in finding robust and efficient computational techniques to find approximate solutions.

The study of the mathematical aspects of the problems in this area were pioneered in the 1970s by E. H. Lieb and coworkers. P.-L. Lions and collaborators, from the 1980s on, have made major contributions to the field. On the other hand, the need of efficient software able to simulate large systems calls for a definite enhancement of the computational aspects of this theory. It was now due time for such a workshop, gathering leading international researchers with different scientific backgrounds: mathematics (nonlinear analysis, PDEs, variational methods),

mathematical physics, scientific computing (numerical analysis, large-scale optimization), theoretical chemistry, biochemistry, materials science, ... The workshop was an opportunity to make a state-of-the art review of the mathematical knowledge, to draw up a list of the potential practical applications and the challenges to overcome in the near future.

This workshop brought together leading figures from the computational quantum chemistry and applied math communities. These are two communities that rarely find themselves at the same conference. It was attended by 47 people, most of them well-known researchers in the field plus some younger researchers. Participants from the chemistry side included experts in density functional theory, quantum Monte Carlo techniques, and quantum dynamics. There were several "hot" topics discussed prominently at the workshop. Among them, the existence and the computation of the optimized effective (OEP) potential in DFT perhaps took central stage. Remarkably, there was enough critical mass of researchers and discussion time to conclude at this point that the existence and uniqueness of this OEP is far from certain. The current methods used in practice for its calculation have shortcomings and there is still lots of room for improvement. Among the mathematicians, half were nonlinear PDE specialists and mathematical physicists and another half, numerical analysts and experts in computational issues.

There were 8 review talks opening the various sections in which the workshop was divided : general models and methods, numerics and approximation, time evolutions problems, density functional and OEP models, control and controllability, relativistic models and quantum Monte Carlo simulations. Every section consisted of the opening (longer) review talk plus some shorter contributions, presenting various, complementary, aspects of the subject.

The talks presented a very large view of the field and this both from the chemistry and from the mathematics viewpoint. The models that are nowadays more popular and used were discussed in depth. The mathematical tools to analyse those models and compute approximate solutions were discussed and already existing applications were described. General numerical methods to analyze a priori or a posteriore errors were presented and discussed in the framework of quantum theory. Many of the talks were not only presentations of existing results but also of the limitations of the current knowledge and description of the most important needs.

In the evenings, after dinner, three round tables were organized in order to foster interactions and discussions on future subjects of interest, on the possibilities of further interaction betweeen mathematics and quantum chemistry and on the modelling and the methodology nowdays available and future prospects. The precise subjects of the round tables were : "Optimized Effective Potentials in DFT", "Developing fruitful interactions at the theoretical level" and "Interactions between chemists and numerical analysts". The three evenings gave us an excellent opportunity to discuss very openly about what is done and what is missing in the present theories and practice.

Based on the feedback already received from participants, we consider the organization of such a workshop equally beneficial for mathematicians and chemists. We hope other workshops in the same spirit will be organized in the near future.

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Workshop: Mathematical and Numerical Aspects of Quantum Chemistry Problems

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Abstracts

A few aspect of QMC for molecules

Michel Caffarel

(joint work with R. Assaraf, A. Khelif, A. Scemama, A. Ramírez-Solís)

In this talk a number of recent works aimed at improving quantum Monte Carlo (QMC) approaches for molecular structure are reported.

1. Improved one-particle properties

First, a recent proposal to greatly increase the efficiency of Monte Carlo calculations of one-body properties (*e.g.* charge and spin densities) is presented. The general idea is to construct an "improved" estimator whose average is identical to the desired average but with a much smaller variance.[1, 2, 3]

In the case of the charge density, $\rho(\mathbf{r})$, the standard estimator has the following form

$$(1) \qquad \rho(\mathbf{r}) = \langle \sum_{i=1}^{N} \delta(\mathbf{r}_i - \mathbf{r}) \rangle_\Pi$$

where N is the number of particles (here, electrons) and Π the underlying probability density sampled by Monte Carlo. Our proposed improved estimator is

$$(2) \qquad \rho(\mathbf{r}) = -\frac{1}{4\pi} \sum_{i=1}^{N} \langle [\frac{1}{|\mathbf{r}_i - \mathbf{r}|} - g] \frac{\nabla_i^2(f\Pi)}{\Pi} \rangle_\Pi,$$

where the two functions f and g play the role of auxiliary quantities. They are introduced to decrease as much as possible the variance of the density estimator. As with any optimization problem, there is no universal strategy for choosing f and g. However, the guiding principle is to identify the leading sources of fluctuations and, then, to adjust the auxiliary functions to remove most of them.

Let us emphasize that this approach is not limited to QMC calculations; our estimator can be readily used in any type of Monte Carlo simulation (*e.g.* Monte Carlo for classical thermodynamics). Furthermore and in sharp contrast with the usual estimator based on the regularization of the delta-function on a grid, our expression leads to accurate estimates of the density at any point in space, even in the regions never visited during the Monte Carlo simulation (*e.g.*, in the large-distance regime). This property is particularly interesting when a global knowledge of the density map is searched for.

Here, we present an application to the water dimer for which we have been able to compute a smooth and accurate map of the charge density for a large number of grid points (51x51x51=132651 points). Remark that such a calculation would be vastly more difficult with the standard approach. Details of the method can be found in Ref.[4].

2. The fermion Monte Carlo method revisited

A second work presented here concerns a detailed mathematical study of a recent proposal by Kalos *et al.*[6] -the Fermion Monte Carlo (FMC) method- to solve the "Fermion-sign" problem. This problem is presently considered as one of the most important challenge in computational physics. In short, the FMC method is based on the use of two types of walkers simulating the positive and negative parts of the signed wavefunction. The "positive" and "negative" walkers are correlated so that to meet with a high probability and, whenever they meet, a cancellation step is done. We have performed a careful mathematical analysis of the various aspects of the method. We have shown that FMC is indeed *exact*. However, the method is still *unstable* but with a weaker instability. We have proved that the statistical error δE on the energy behaves as $\delta E \sim \frac{e^{(E_F - \tilde{E}_B)N}}{\sqrt{N}}$ where E_F is the fermi ground-state energy, E_B the bose ground-state energy, and $\tilde{E}_B$ some effective bose energy verifying $E_F \geq \tilde{E}_B > E_B$. Note that the exact QMC methods proposed so far can be viewed as unstable approaches with $\tilde{E}_B = E_B$ (no change of the Bose state). To summarize, FMC is as an exact fermion method having an attenuate exponential blow up of statistical fluctuations at large simulation times. However, the pathological behavior of the error as a function of the number of fermions (rapid increase of the Bose-Fermi gap) is still present. Details about this study can be found in Ref.[5].

3. Fixed-node error in chemistry

A last work presented here concerns the role played by the "fixed-node" error in the chemistry of real systems. It is usually said that the fixed-node approximation is very good. For total energies it is certainly true since, in general, the fixed-node error represents only a few percents of the total correlation energy (defined as the difference between the exact and the Hartree-Fock energies), a result which is considered as very good in computational chemistry. However, we emphasize that such impressive result does not necessarily extend to the calculations of the *very small differences* of energies involved in chemistry. In other words, the small errors in total energies can lead to large uncontrolled errors in the very small energy differences we are interested in. When computing differences of energies with standard *ab initio* wavefunction-based and DFT methods a large cancellation of sytematic errors is at work (use of a common basis set and common molecular orbitals not involved in the chemical process). This is not the case in QMC simulations. Let us present two applications illustrating this important point.

A. Dissociation barrier of O_4
We are interested in the process: O_4 (singlet metastable state) $\Leftrightarrow$ O_4 [singlet transition state (TS)] $\Leftrightarrow$ 2 O_2 (stable triplet state). Experimental results indicate that the dissociation barrier associated with $O_4 \Rightarrow O_4$(TS) is probably greater than 10 kcal. Sophisticated *ab initio* calculations [CCSD(T), ACPF, etc.] lead to a barrier of about 8-9 kcal. Our fixed-Node DMC calculations give a barrier of 26.2 ± 2.9 kcal with SCF nodes, and 12.7 ± 3.7 kcal with MCSCF nodes. As seen,

the value of the dissociation barrier is very dependent on the nature of the nodes ("monoconfigurational" or "multiconfigurational").

B. Fixed-Node DMC for Cr_2.

The chromium dimer is known to be a very difficult problem for all computational chemistry approaches. The experimental binding energy of this molecule is $\sim$ -0.056 a.u. The SCF binding energy (basis set= [20s12p9d5f]) is about +0.795 a.u. In other words the "SCF molecule" does not exist (unbound by a large amount). Our fixed-node DMC calculation obtained with SCF nodes leads to: $E_0(Cr_2)$-2 $E_0(Cr)$ = +0.01(3). Cr_2 is therefore found to be unbound (or slightly bound) at the fixed-node DMC level with "monoconfigurational" nodes, although a large part of the correlation energy is recovered. Clearly, in this case, multiconfigurational trial wavefunctions are called for. This result illustrates the importance of correctly describing the nodal structure of the exact wavefunctions when applying FN-DMC. Details about fixed-node simulations for "difficult" systems of quantum chemistry can be found in [7, 8].

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Numerical analysis for electronic structure calculations: an overview

ERIC CANCÈS

The first part of my talk will be devoted to the numerical simulation of the Hartree-Fock model for molecular systems of moderate size (up to a few hundreds of electrons). After recalling the structure and the main mathematical properties of the Hartree-Fock model, I will present some theoretical results on Self-Consistent Field (SCF) algorithms [1]. In particular, I will analyze the failures of the Roothaan algorithm [2], and introduce the Optimal Damping Algorithm [3, 4]

(ODA), which enjoys interesting features. First, it is proved to monotonically converge toward a critical point of the Hartree-Fock energy satisfying the *Aufbau* principle. Second, it is very robust, in the sense that, in most cases, it converges toward the (hopefully) global minimum, even for crude initial guesses. An improvement of ODA, namely the EDDIS algorithm [5], will also be presented. Both ODA and EDIIS can be extended to Kohn-Sham models [6, 7].

In the second part of my talk, I will describe a variational multilevel domain decomposition method for solving the linear subproblem arising in Hartree-Fock and Kohn-Sham calculations, for large size molecular systems (hundred thousands of electrons). This method has been introduced in [8]. An improvement of it has been proposed in [9]. This method iterates between local fine solvers and global coarse solvers, in the spirit of the domain decomposition methods used in other fields of the engineering sciences. Using this approach, calculations have been successfully performed on several linear polymer chains containing up to 100,000 atoms and 380,000 atomic orbitals. Both the computational cost and the memory requirement scale linearly with the number of atoms.

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Models for laser-matter interaction in the high-frequency regime

FRANÇOIS CASTELLA

(joint work with E. Dumas)

We consider a laser beam in the three dimensional space $\mathbb{R}^3$, sent in a collection of identical atoms (say in a gas, or in an optical fiber). We let the laser propagate over long distances with respect to the laser's wavelength: the regime under study naturally is a high-frequency regime. We wish to describe, along the high-frequency asymptotics, the laser-matter interaction.

One basic model for laser-matter interaction is the so-called Maxwell-Bloch system (see *e.g.* [10], [9], see also [1]). Its unknowns are the electromagnetic field $(E, B) = (E, B)(t, x, y, z) \in \mathbb{R}^6$, and the so-called density-matrix $\rho = \rho(t, x, y, z)$, which is an operator on $L^2(\mathbb{R}^3)$ for each value of time t and space (x, y, z). The density matrix ρ describes the state of matter, while the field (E, B) describes the state of the laser signal, at (t, x, y, z). This being settled, the Maxwell-Bloch system consists on the one hand of a Maxwell equation for the electro-magnetic field. It reads, in convenient units,

$$(1) \qquad \partial_t B + \operatorname{curl} E = 0,$$
$$\partial_t E - \operatorname{curl} B = -\partial_t P.$$

Here P is the so-called polarisation: it describes how matter responds to the presence of the laser field (E, B). In essence, P is proportional with ρ, *i.e.* it depends linearly on the state of matter. The system also includes a Schrödinger-like equation for ρ, namely the Bloch equation, which reads, in convenient units,

$$(2) \qquad \partial_t \rho = -i \left[H_{\text{atom}} + H_{\text{field}} , \rho \right] + \text{dissipation}.$$

Here, $[.,.]$ denotes a commutator (between operators), H_{atom} is the elementary atomic Hamiltonian, while H_{field} is the Hamiltonian created by the laser field and acting on the collection of atoms. In essence, H_{field} is proportional with the field E (in the so-called dipolar approximation). The dissipative term, whose very value is not made precise here (see [7], see also [2]), expresses the natural trend of the atoms to relax towards equilibrium states of H_{atom}.

The system (1)-(2) with unknowns (E, B, ρ) is nonlinear and coupled: the nonlinearity is essentially proportional with the product $E \times \rho$.

Due to the high-frequency regime, we consider a scaled form of (1)-(2): it is valid for sufficiently weak lasers (so that the optical properties of matter are *not* modified by the laser field), and propagating over sufficiently long time scales (so that both propagative and dispersive effects do take place). We also restrict our attention to laser beams, propagating in one distinguished direction, say in the direction x (so that the laser's extension in the tranverse (y, z) direction is much smaller than its extension in the propagative x direction).

We prove in [7] that the complete, scaled, Maxwell-Bloch system (6 unknowns for the field, and one operator-valued unknown for the atoms, all unknowns being propagated in the three-dimensional space) is asymptotically well described,

in this regime, by a single, scalar, Schrödinger equation for the asymptotic field $\mathcal{E} = \mathcal{E}(t, x, y, z)$, of the form

$$(3) \qquad \underbrace{(\partial_t - \partial_x)\,\mathcal{E}}_{\text{propagation in the direction } x} \quad - \quad \underbrace{i\Delta_{y,z}\mathcal{E}}_{\text{dispersive effects in the transverse direction}} \quad = \text{source.}$$

(Here, $\mathcal{E}$ is the limiting envelope of the original field E). Up to the source term (described below), equation (3) is very reminiscent of the standard paraxial approximation in laser propagation. On top of that, matter is eventually well-described by a scalar unknown $N(t, n)$ (instead of the operator $\rho(t)$), indexed by the atoms' energy levels n. The quantity $N(t, n)$ is the probability, at time t, to find an atom in the n-th eigenstate of the atomic Hamiltonian H_{atom}. It satisfies a Boltzmann like equation, of the form

$$(4) \qquad \partial_t N(t, n) = \sum_k \sigma(n, k)\,[N(t, k) - N(t, n)],$$

where $\sigma(n, k) \geq 0$ is a transition rate, describing the probability that a given atom "jumps" from the n-th eigenstate to the k-th eigenstate, under the action of the external field $\mathcal{E}$ (absorption or emission of a photon). Last, it is proved that the transition rate σ is proportional with $|\mathcal{E}|^2$, namely to the laser's power, while the source term in (3) is proportional with the product $\mathcal{E} \times N$.

Technically speaking, this result involves tools from three scales geometric optics [8] (see also [5]), as well as some small divisors estimates.

The present study completes, in the fully nonlinear situation, a previous study valid in the case where the laser signal (E, B) is considered given at once (rather than given through the resolution of a Maxwell system), see [3, 4]: in that case the techniques are quite different, since averaging tools from the analysis of ordinary differential equations are used (see [12]).

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Relativistic hydrogenic atoms in strong magnetic fields

Jean Dolbeault

(joint work with M. J. Esteban, and M. Loss)

Abstract. *In the Dirac operator framework we characterize and estimate the ground state energy of relativistic hydrogenic atoms in a constant magnetic field and describe the asymptotic regime corresponding to a large field strength using Landau levels. We also define and estimate a notion of critical magnetic field.*

The Dirac operator for a hydrogenic atom in the presence of a constant magnetic field B in the x_3-direction is given by

$$H_{B,\nu} := H_B - \frac{\nu}{|x|} \quad \text{with} \quad H_B := \alpha \cdot \left[\frac{1}{i} \nabla + \frac{1}{2} B(-x_2, x_1, 0) \right] + \beta$$

where α_1, α_2, α_3 and β are 4×4 complex matrices, whose standard form in 2×2 blocks is

$$\beta = \begin{pmatrix} \mathbb{I} & 0 \\ 0 & -\mathbb{I} \end{pmatrix}, \quad \alpha_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix} \qquad k = 1, 2, 3 \, .$$

Here we have used the notations $\mathbb{I} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ and σ_k are the Pauli matrices:

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} .$$

The coupling constant $\nu = Z\alpha$ is supposed strictly less than 1, Z is the nuclear charge number and $\alpha \approx 1/137.037$ is the Sommerfeld fine-structure constant. See [7] for more details on Dirac's equation.

The ground state energy $\lambda_1(\nu, B)$ is defined as the smallest eigenvalue in the gap $(-1, 1)$ of $H_{B,\nu}$. As the value of B increases, $\lambda_1(\nu, B)$ converges to -1, which is achieved for some critical field strength $B(\nu)$. Our first main result is based on a min-max characterization of the ground state energy and provides a rough non perturbative estimate of $B(\nu)$:

$$\frac{4}{5\,\nu^2} \; \leq \; B(\nu) \; \leq \; \min\left(\frac{18\,\pi\,\nu^2}{[3\,\nu^2 - 2]_+^2} \, , \, e^{C/\nu^2} \right) .$$

We are indeed able to extend the results of [4] to the case with a constant magnetic field. One of the main ingredient is the characterization of $\lambda_1(\nu, B)$ as

the infimum of $\lambda[\phi, \nu, B]$ on a set of admissible two components spinors ϕ, where $\lambda = \lambda[\phi, \nu, B]$ is either the unique solution to

$$0 = J[\phi, \lambda, \nu, B] := \int_{\mathbb{R}^3} \left(\frac{|P_B \phi|^2}{1 + \lambda + \frac{\nu}{|x|}} + (1 - \lambda) |\phi|^2 - \frac{\nu}{|x|} |\phi|^2 \right) d^3 x$$

or $\lambda[\phi, \nu, B] = -1$ if $J[\phi, -1, \nu, B] \leq 0$. Here we use the notations $P_B := -i\,\sigma \cdot (\nabla - i\, A_B(x))$, $A_B(x) := \frac{B}{2}(-x_2, \, x_1, \, 0)$. This problem is related to the eigenvalue problem for $H_{B,\nu}$ as follows. If $\psi = \binom{\phi}{\chi}$ is an eigenfunction with eigenvalue λ, the eigenvalue equation is equivalent to $P_B \chi + \phi - \frac{\nu}{|x|}\phi = \lambda \phi$ $P_B \phi - \chi - \frac{\nu}{|x|}\chi = \lambda \chi$ and we can eliminate the lower component χ. The equation for ϕ is then a critical point of $J[\phi, \lambda, \nu, B]$, with critical vlaue 0.

We also study the asymptotics of $B(\nu)$ as $\nu \to 0$ using the notion of lowest relativistic Landau level which leads to a one dimensional effective theory. This effective theory can be analyzed in great detail and allows to calculate the ground state energy $\lambda_1^{\mathcal{L}}(\nu, B)$ of the magnetic Dirac–Coulomb equation in the lowest relativistic Landau level. It is given by the variational problem

$$\lambda_1^{\mathcal{L}}(\nu, B) := \inf_{f \in C_0^\infty(\mathbb{R}, \mathbb{C}) \setminus \{0\}} \lambda^{\mathcal{L}}[f, \nu, B] \ ,$$

where $\lambda = \lambda^{\mathcal{L}}[f, \nu, B]$ is defined by

$$\lambda \int_{\mathbb{R}} |f(z)|^2 \, dz = \int_{\mathbb{R}} \left(\frac{|f'(z)|^2}{1 + \lambda + \nu\, a_0^B(z)} + (1 - \nu\, a_0^B(z)) |f(z)|^2 \right) dz$$

and $a_0^B(z) := B \int_0^{+\infty} \frac{s\, e^{-\frac{1}{2} B s^2}}{\sqrt{s^2 + z^2}} \, ds$. For B not too small and ν not too large, we prove the estimate $\lambda_1^{\mathcal{L}}(\nu + \nu^{3/2}, B) \leq \lambda_1(\nu, B) \leq \lambda_1^{\mathcal{L}}(\nu - \nu^{3/2}, B)$.

The one dimensional $\lambda_1^{\mathcal{L}}(\nu, B)$ problem, although not trivial, is simpler to calculate than the $\lambda_1(\nu, B)$ problem and allows to prove that $\lim_{\nu \to 0} \nu \log(B(\nu)) = \pi$. The relativistic Dirac-Coulomb operator in a constant magnetic field differs from the corresponding Pauli equation studied in [1] by several aspects. First of all, imposing that $\lambda_1(\nu, B)$ lies in the gap $(-1, 1)$ limitates the strength of the admissible magnetic field. Next the natural units in which the field is measured, or the characteristic parameters that one uses to adimensionalize the equation, are not the same. Looking at min-max levels makes the computations rather involved and significantly different from the ones based on Raleigh quotients in the non-relativistic case. Introducing Landau levels in such a framework requires new tools. Hence it looks rather difficult to establish an asymptotic expansion of $B(\nu)$ even as $\nu \to 0$. Surprisingly, our lower estimate of the critical magnetic field converges to some finite positive limit in the other limiting regime, that is for $\nu \to 1$. This clearly emphasizes the non-perturbative character of the method.

From a physical point of view, the model is motivated by trying to guess the possibility of spontaneous pair creation in strong external fields. The Dirac-Coulomb operator allows to take into account simultaneously the Coulomb potential and the magnetic field in a truly relativistic framework. As far as we know and with all precautions needed to argue on Dirac's equation, this is a significant step in

evaluating critical magnetic fields. From a practical point of view, it seems that magnetic fields that can compare with the estimates we have found can be expected to exist only in neutron stars during their gestation and in some special kind of neutron stars called magnetars, see [6, 5]. Apparently atoms may persist up to about $Z = 40$ near the surface of such stars. Although not incompatible with measured values of the field, our bounds suggest that the magnetic field is not strong enough for pair creation. An accurate numerical scheme is currently being investigated, [2]. More details on the theoretical aspects can be found in [3].

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Weak interaction limit for a model of nuclear matter
BERNARD DUCOMET
(joint work with C. Bardos, F. Golse, A.D. Gottlieb and N.J. Mauser)

We consider a simplified model of nuclear matter given by the renormalized hamiltonian

$$H_N = \sum_j \mathcal{L}_j + \frac{1}{N-1} \sum_{j,k} V_{ij}^{(2)} + \frac{1}{(N-1)(N-2)} \sum_{j,k,\ell} V_{jk\ell}^{(3)},$$

defined on the N-particle space built on a one-particle Hilbert space $\mathfrak{H}$ including spin (spin up $\sigma = 1/2$ and spin down $\sigma = -1/2$) and isospin (neutron $\tau = -1/2$ and proton $\tau = 1/2$) degrees of freedom. We are interested in the weak coupling limit of the system (in the sense of Spohn [3]), corresponding to the large N limit of H_N.

Aside the one-body contribution, H_N contains specific 2-body and 3-body contributions. The one-body term includes the kinetic operator together with the intrinsic spin-orbit contribution

$$(1) \qquad \mathcal{L} := -\frac{\hbar^2}{2m}\Delta + w_{ls} \; L \cdot S.$$

where the one-particle angular momentum operator L for each particle, with components L_α for $\alpha = 1, 2, 3$ is

$$L_\alpha := -i \left(r_\beta \frac{\partial}{\partial r_\gamma} - r_\gamma \frac{\partial}{\partial r_\beta} \right),$$

with (α, β, γ) is a cyclic permutation of $(1, 2, 3)$, and the spin operators S_3, S_+ and S_- are defined by $(S_3 \phi)(r, \sigma, \tau) := \hbar \sigma \, \phi(r, \sigma, \tau)$, for $\sigma \in \{-1/2, 1/2\}$,

$$(S_+ \phi)(r, \sigma, \tau) := \hbar \sqrt{(1/2 + \sigma)(3/2 - \sigma)} \, \phi(r, \sigma - 1, \tau), \quad \text{for } \sigma \in \{-1/2, 1/2\},$$

and

$$(S_- \phi)(r, \sigma, \tau) := \hbar \sqrt{(1/2 - \sigma)(3/2 + \sigma)} \, \phi(r, \sigma + 1, \tau), \quad \text{for } \sigma \in \{-1/2, 1/2\},$$

where one checks that $(S_+ \phi)(r, \sigma = -1/2, \tau) = (S_- \phi)(r, \sigma = 1/2, \tau) = 0$, and the three components S_α, for $\alpha = 1, 2, 3$, of the spin operator S used in the spin-orbit interaction are finally defined by $S_1 = \frac{1}{i}(S_+ + S_-)$, $S_2 = -\frac{1}{i}(S_+ - S_-)$ and S_3.

The isospin operators T_1, T_2 and T_3 are defined exactly by the same expressions, just by exchanging the respective roles of spin σ and isospin τ.

Concerning the k-body contributions with $k = 2, 3$, as the nucleon-nucleon force cannot yet be derived from the QCD theory of strong interactions, several *effective interactions* taking into account the medium effects have been built [1]. We concentrate below on the Gogny finite-range D1 interaction [2].

For a two nucleons system $(1, 2)$, let us define the two-body spin exchange operator P_σ, acting on simple states by

$$P_\sigma \, \phi(r_1, \sigma_1, \tau_1) \phi(r_2, \sigma_2, \tau_2) = \phi(r_1, \sigma_2, \tau_1) \phi(r_2, \sigma_1, \tau_2),$$

and the two-body isospin exchange operator P_τ acting in a similar way on the variable τ. Then, the two-body contribution $V^{(2)}$ is given by

$$(2) \qquad V_{ij}^{(2)} = \sum_{n=1}^{2} e^{-\frac{|r_i - r_j|^2}{\mu_n}} \left(w_n + b_n P_\sigma - h_n P_\tau - m_n P_\sigma P_\tau \right),$$

where the sum involves the operators P_σ, which exchanges spins σ_i and σ_j, P_τ which exchanges isospins τ_i and τ_j.

Finally, the three-body term $V^{(3)}$ has a purely spatial smeared contribution

$$(3) \qquad V_{ijk}^{(3)} = t_3 e^{-\frac{|r_i - r_j|^2 + |r_j - r_k|^2}{\mu_2}} \, I.$$

In these expressions w_n, b_n, h_n, m_n, t_3 and the nuclear ranges μ_n are adjusted to experimental data, with precise values (see [2]).

In order to formulate the problem in the density-operator language, we note $\mathcal{A}_N$ the antisymmetric subspace of $\mathfrak{H}_N$ defined by using unitary permutation operators on $\mathfrak{H}_N$: if, for any π in the group $\mathfrak{G}_N$ of permutations of $\{1, 2, \ldots, N\}$, one considers the permutation operator U_π as $U_\pi(\xi_1 \otimes \ldots \otimes \xi_n) = \xi_{\pi^{-1}(1)} \otimes \ldots \otimes \xi_{\pi^{-1}(n)})$, then $\mathcal{A}_N := \{\psi \in \mathfrak{H}_N \ : \ U_\pi \psi = \operatorname{sgn}(\pi) \psi \quad \forall \pi \in \mathfrak{G}_N\}$. A density operator D on $\mathfrak{H}_N$ is sait to be symmetric if it commutes with every permutation operator U_π, and we also note $\Sigma_n := n! P_{\mathcal{A}_N}$, where $P_{\mathcal{A}_N} = \frac{1}{N!} \sum_{\pi \in \mathfrak{G}_N} \operatorname{sgn}(\pi) U_\pi$ is the projector whose range is $\mathcal{A}_N$.

For $n \leq N$, the nth partial trace $T_{:n}$ of $T \in \mathcal{T}(\mathfrak{H}^{\otimes N})$ may be defined for any orthonormal basis $\mathcal{O}$ of $\mathfrak{H}$ by

$$(4) \quad \langle T_{:n} w, x \rangle = \sum_{j=1}^{N-n} \sum_{y_j \in \mathcal{O}} \Big\langle T(w \otimes y_1 \otimes \cdots \otimes y_{N-n}), \ (x \otimes y_1 \otimes \cdots \otimes y_{N-n}) \Big\rangle$$

for any $w, x \in \mathfrak{H}^{\otimes n}$.

To compare the N-body dynamics on $\mathfrak{H}_N$ to the 1-body dynamics on $\mathfrak{H}$, we set the definition (reminiscent of an explicit formula valid for Slater determinants)

Definition 1. *For each N, let D_N be a symmetric density operator on $\mathfrak{H}_N$. The sequence $\{D_N\}$ **has Slater closure** if, for each fixed n, $\lim_{N \to \infty} \big\| D_{N:n} - D_{N:1}^{\otimes n} \Sigma_n \big\|_{tr} = 0$,*

If $\mathcal{L}^{(N)}$ denotes the previous one body potential $-\frac{\hbar^2}{2m}\Delta + w_{ls} \ L \cdot S$ acting on a single particle, the free motion of the jth particle is given by the (unbounded) operator on on $\mathfrak{H}^{\otimes N}$ $\mathcal{L}_j^{(N)} = I^{\otimes j-1} \otimes L^{(N)} \otimes I^{\otimes N-j}$, where I denotes the identity operator on $\mathfrak{H}$.

In the same stroke, if the k-body potential $V^{(k)}$ is a bounded operator on $\mathfrak{H}^{\otimes k}$ that commutes with the transposition operator U_π, for any $\pi \in \mathfrak{G}_k$, the operator $V_{i_1,i_2,\dots i_k}^{(k)}$ on $\mathfrak{H}^{\otimes N}$ is equal to $V_{ij} = U_\pi^* V_{1,2,\dots k}^{(m)} U_\pi$ where π is any permutation in $\mathfrak{G}_N$ with $j = \pi(i_j)$ for $j = 1, \dots m$, and

$$V_{1,2,\dots k}^{(k)} (x_1 \otimes x_2 \otimes \cdots \otimes x_N) = V^{(k)}(x_1 \otimes \dots \otimes x_k) \otimes \cdots \otimes x_N.$$

Then the renormalized *N-particle Hamiltonian* operator on $\mathfrak{H}_N$

$$(5) \ H_N = \sum_{1 \leq j \leq N} \mathcal{L}_j^{(N)} + \frac{1}{N-1} \sum_{1 \leq i < j \leq N} V_{ij}^{(2)} + \frac{1}{(N-1)(N-2)} \sum_{1 \leq i < j < k \leq N} V_{ijk}^{(3)},$$

leads to the von Neumann equation for the N-particle density operator $D_N(t)$

$$i\hbar \frac{d}{dt} D_N(t) = \sum_{1 \leq j \leq N} \big[\mathcal{L}_j^{(N)}, D_N(t) \big] + \frac{1}{N-1} \sum_{1 \leq i < j \leq N} \big[V_{ij}^{(2)}, D_N(t) \big]$$

$$(6) \qquad\qquad + \frac{1}{(N-1)(N-2)} \sum_{1 \leq i < j < k \leq N} \big[V_{ijk}^{(3)}, D_N(t) \big].$$

The time-dependent Hartree-Fock (TDHF) equation for a density operator $F(t)$ on $\mathfrak{H}$ is

$$(7) \qquad i\hbar \frac{d}{dt} F(t) = \big[L^{(N)}, \ F(t) \big] + \big[V^{(2)}, \ F_2^-(t) \big]_{:1} + \big[V^{(3)}, \ F_3^-(t) \big]_{:1},$$

where $F_n^-(t) = F(t)^{\otimes n} \Sigma_n$.

The relationship between the N-particle system and the corresponding TDHF equation is given by the following result [7].

Theorem 1. *For each N, let $D_N(t)$ a solution to (6) whose initial value $D_N(0)$ is a symmetric density. Let $F^{(N)}(t)$ be the solution of the TDHF equation (7) whose initial value is $F^{(N)}(0) = D_{N:1}(0)$.*

If $\{D_N(0)\}$ has Slater closure then $\{D_N(t)\}$ has Slater closure and for all $t > 0$

$$\lim_{N \to \infty} \left\| D_{N:1}(t) - F^{(N)}(t) \right\|_{tr} = 0.$$

The proof consists in a careful study of the deviation between two hierarchies: the first one analogous to the BBGKY hierarchy for the reduced density operators $D_{N:n}(t)$ and the second built on the factorized density operators $F^{\otimes n} \, \Sigma_n$.

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Regularity properties of molecular eigenfunctions and densities

Soren Fournais

(joint work with M. Hoffmann-Ostenhof, T. Hoffmann-Ostenhof, and T. Østergaard Sørensen)

1. Introduction and results

Suppose given L fixed nuclei with the position and charge of the ℓ'th nucleus being $X_\ell \in \mathbb{R}^3$ and $Z_\ell \in \mathbb{R}_+$. Let H be the non-relativistic Schrödinger operator of the corresponding N-electron molecule in the fixed nucleus approximation, i.e.,

$$(1) \qquad H = \sum_{j=1}^{N} \left(-\Delta_j - \sum_{l=1}^{L} \frac{Z_\ell}{|x_j - X_\ell|} \right) + \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|}.$$

Here the $x_j = (x_{j,1}, x_{j,2}, x_{j,3}) \in \mathbb{R}^3$, $j = 1, \dots, N$, denote the positions of the electrons, and the Δ_j are the associated Laplacians so that $\Delta = \sum_{j=1}^{N} \Delta_j$ is the $3N$-dimensional Laplacian. Let $\mathbf{x} = (x_1, x_2, \dots, x_N) \in \mathbb{R}^{3N}$ and let $\nabla = (\nabla_1, \dots, \nabla_N)$ denote the $3N$-dimensional gradient operator. The operator H is selfadjoint with operator domain $\mathcal{D}(H) = W^{2,2}(\mathbb{R}^{3N})$ and form domain $\mathcal{Q}(H) = W^{1,2}(\mathbb{R}^{3N})$.

We have for some time (see [3, 4, 5, 6, 7, 8, 12] and also [11] for earlier work) been interested in the study of the regularity of solutions ψ to the corresponding eigenvalue equation

$$(2) \qquad\qquad H\psi = E\psi, \qquad E \in \mathbb{R}.$$

We will here give a quick overview of some of the main results obtained with pointers to relevant literature. Due to the obvious limitations of space, neither the review of results nor the list of references can be exhaustive.

Any analysis of this question must start with the observation that since (2) is an elliptic PDE, solutions will be very regular in most of $\mathbb{R}^{3N}$. More precisely, let Σ be the set where the coefficients of the operator H are singular,

$$\Sigma := \big\{\mathbf{x} \in \mathbb{R}^{3N} \mid \textstyle\prod_{j,l}|x_j - X_\ell| \prod_{j<k}|x_j - x_k| = 0\big\}.$$

Then, by elliptic regularity, eigenfunctions will be real analytic in $\mathbb{R}^{3N} \setminus \Sigma$. The celebrated 'Kato cusp condition' [14] states that on Σ, ψ will have certain specific singularities. Our first result, Theorem 1, is an improved version of Kato's result. It is also related to the work on 'Fock expansions' [2, 15].

Theorem 1 (See [6]).
Define $y_{j,\ell} := x_j - X_\ell$,

$$(3) \qquad F_2(\mathbf{x}) = -\sum_{l=1}^{L}\sum_{j=1}^{N} Z_\ell |y_{j,l}|/2 + \sum_{1 \le j < k \le N} |x_j - x_k|/4,$$

$$(4) \qquad F_3(\mathbf{x}) = \frac{2-\pi}{12\pi}\sum_{l=1}^{L} Z_\ell \sum_{1 \le j < k \le N} (y_{j,l} \cdot y_{k,l})\ln(|y_{j,l}|^2 + |y_{k,l}|^2).$$

Then any solution ψ to equation (2) can be factorized as

$$(5) \qquad\qquad \psi = e^{F_2 + F_3}\phi_3 \qquad with\ \phi_3 \in C^{1,1}(\mathbb{R}^{3N}).$$

Furthermore, the representation (5) is optimal—$C^{1,1}$ is the best possible regularity for a product 'Ansatz'—see [6] for details.

Having a description of the structure of the leading singularities of the eigenfunction ψ we now turn to the (one-electron) density. Given $\psi \in L^2(\mathbb{R}^{3N})$ we define $\rho \in L^1(\mathbb{R}^3)$ as

$$(6) \qquad\qquad \rho(x) = \sum_{j=1}^{N}\int_{\mathbb{R}^{3N}}|\psi(\mathbf{x})|^2\delta(x_j - x)\,d\mathbf{x}.$$

The cusp condition for the eigenfunction has been generalised to the density ρ in [16, 13] (see (9) below for an improvement of that result). Away from the nuclei one might expect that the integrations in (6) will smooth out the singularities of ψ to some extent. This turns out to be very much the case.

In order to study pointwise properties of ρ it seems necessary to assume some kind of decay of the eigenfunction ψ. Since molecular eigenfunctions generally decay exponentially (see [1, 9] and also [10]) it is natural—and we will do so below without explicit reference thereto—to assume exponential decay of ψ.

In the study of the regularity of ρ it is useful to have a differential equation for the density. Such an equation was derived in [12] and follows from (2) by using the identity

$$(7) \qquad \sum_{j=1}^{N} \int_{\mathbb{R}^{3N}} \overline{\psi(\mathbf{x})}(H - E)\psi(\mathbf{x})\delta(x_j - x)\,d\mathbf{x} = 0\,,$$

and carrying out the integration. From (7) one finds the (inhomogeneous one-particle Schrödinger) equation for ρ,

$$(8) \qquad -\frac{1}{2}\Delta\rho - \frac{Z}{|x|}\rho + h = 0 \quad \text{in} \quad \mathbb{R}^3\,.$$

Here h is an explicit function (given in terms of ψ) and it is feasible to prove regularity of h, which by means of (8) and elliptic theory implies regularity of ρ.

Theorem 2 (See [3, 4, 5, 7]).
Let $\psi \in L^2(\mathbb{R}^{3N})$ be a solution to (2) and let ρ be the associated density. Then ρ is real analytic on $\mathbb{R}^3 \setminus \{X_1, \ldots, X_L\}$. Furthermore, ρ satisfies ('cusp condition')

$$(9) \qquad \rho(x) = \mu(x)\exp(-\textstyle\sum_{l=1}^{L} Z_\ell |x - X_\ell|) \qquad \text{with } \mu \in C^{1,1}(\mathbb{R}^3).$$

If one wants to understand the singularities of ρ at the nuclei further, one possibility is to study the spherically averaged density (see also [7] for an alternative). This makes most sense for atoms, so we assume that $L = 1$, $X_1 = 0$ and define

$$(10) \qquad \widetilde{\rho}(r) = \int_{\mathbb{S}^2} \rho(r\omega)\,d\omega\,.$$

Theorem 3 (See [8, 12]).
Let ψ be an atomic eigenfunction with eigenvalue E and suppose that E is below the essential spectrum. Let $\widetilde{\rho}$ be the spherically averaged density associated to ψ. Then $\widetilde{\rho}$ is real analytic on $(0, +\infty)$ and $\widetilde{\rho} \in C^3([0, +\infty))$. Furthermore, we have

$$(11) \qquad \widetilde{\rho}\,'(0) = -Z\widetilde{\rho}(0)\,, \qquad \widetilde{\rho}\,''(0) \geq \frac{2}{3}\,Z^2\widetilde{\rho}(0)\,, \qquad \widetilde{\rho}\,'''(0) \leq -\frac{7}{12}Z^3\widetilde{\rho}(0)\,.$$

The constants in the inequalities in (11) are optimal.

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Mathematical aspects of van der Waals forces

GERO FRIESECKE

(joint work with P. Gardner)

1. Introduction

In this talk we report on our recent mathematical work [Fr06], [FG06], in which we

– discuss how van der Waals forces emerge in a long distance limit as rigorous corrections to the quantum mechanical energy and wavefunction of noninteracting atoms

– evaluate the VdW constant for a pair of hydrogen atoms in closed form, and in particular quantify the contribution from the continuous spectrum missed in the original works of London and coworkers (it turns out to be large, about 40 percent)

– analyse the corrector wave function for hydrogen and prove an explicit angle correlation law which makes quantitative the intuition that the atoms "dynamically polarize each other".

Besides their obvious physical interest, vdW forces are

– not captured by standard approximations of quantum mechanics such as Hartree-Fock- and density functional theory, even in the limit of complete basis sets

– a very good test case to learn something about electron correlation.

2. Born-Oppenheimer potential energy surface

Starting point of the mathematical analysis is the full Born-Oppenheimer two-atom potential energy surface

$$v(|R_A - R_B|) = E_0(H_{A,B}) - \Big(E_0(H_A) + E_0(H_B) \Big)$$

where $H_{A,B}$ is the Hamilton operator of the two-atom system, H_A and H_B are the Hamilton operators of the individual atoms, R_A and R_B are the positions of the atomic nuclei, and E_0 denotes the lowest eigenvalue. Explicitly,

$$H_{A,B} = \sum_{i=1}^{N} \Big(\frac{1}{2} \nabla_{r_i}^2 - \frac{Z_A}{|r_i - R_A|} - \frac{Z_B}{|r_i - R_B|} \Big) + \sum_{i<j} \frac{1}{|r_i - r_j|} + \frac{Z_A Z_B}{|R_A - R_B|},$$

acting on the antisymmetric subspace of $L^2((\mathbb{R}^3 \times \mathbb{Z}_2)^N)$, where Z_A, Z_B are the nuclear charges and $N = Z_A + Z_B$ is the number of electrons. The following well known statement is a rigorous theorem:

Theorem 1 *If H_A and H_B have a zero angular momentum ground state, then as $|R_A - R_B| = R \to \infty$ (at fixed $e = \frac{R_A - R_B}{|R_A - R_B|}$) $v(R) = -c_6 R^{-6} + O(R^{-8})$ for some constant $c_6 > 0$. If the GS is up to spin nondegenerate,*

$$c_6 = \Big\langle H'\Psi^{(0)} \Big| \Big((H^{(0)} - E^{(0)}) \Big|_{\{\Psi^{(0)}\}^\perp} \Big)^{-1} \Big| H'\Psi^{(0)} \Big\rangle,$$

where $H^{(0)}$ is the noninteracting Hamiltonian of the two atoms and

$$H' = \sum_{i=1}^{Z_A} \sum_{j=1}^{Z_B} x_i \cdot D y_j, \quad D = I - 2e \otimes e.$$

The scaling law goes back to fundamental papers by London and coworkers [EL30], [Lo30]. The formula for c_6 is of somewhat later origin (the original workers only considered contributions coming from bound states of the individual atoms but missed out on contributions coming from scattering states). The basic strategy to derive such a result, going back to London et al, is to

1) Taylor-approximate interactions between far particles
2) Treat these approximate interactions via 2nd (or higher) order perturbation theory.

The perhaps most interesting phenomenon here, analyzed first in [Ah76], is that this innocent looking procedure does not lead to a convergent but only an *asymptotic* $1/R$ series for $v(R)$. In other words the error $v(R) - \sum_{j=0}^{N} a_n R^{-n}$ becomes small if N is kept fixed and R becomes large, but not if R is fixed and N becomes large, so at fixed finite R it is not better to include more and more terms in the perturbation series. This has to do with the fact that the approximate Hamiltonians obtained in 1) are negative polynomials in some direction and hence have ground state energy $-\infty$. See [Fr06] for more information and a rigorous proof of Theorem 1.

3. Van der Waals constant

For a pair of hydrogen atoms the van der Waals constant can be evaluated in closed form.

Theorem 2 [FG06]

$$
\begin{aligned}
c_6 = \frac{131072}{3} \Big(& \sum_{n=2}^{\infty} \sum_{n'=2}^{\infty} \frac{n^7(n-1)^{2n-5} n'^7(n'-1)^{2n'-5}}{(n+1)^{2n+5}(n'+1)^{2n'+5}(1-(\frac{1}{2n^2}+\frac{1}{2n'^2}))} \\
& + 2 \sum_{n=2}^{\infty} \int_0^{\infty} \frac{n^7(n-1)^{2n-5} k' e^{-4(\arctan k')/k'}}{(n+1)^{2n+5}(1-e^{-2\pi/k'})(1+k'^2)^5(1+\frac{1}{2}(k'^2-\frac{1}{n^2}))} dk' \\
& + \int_0^{\infty} \int_0^{\infty} \frac{k e^{-4(\arctan k)/k} k' e^{-4(\arctan k')/k'}}{(1-e^{-2\pi/k})(1+k^2)^5(1-e^{-2\pi/k'})(1+k'^2)^5(1+\frac{1}{2}(k^2+k'^2))} dk\, dk' \Big)
\end{aligned}
$$

which evaluates (to 3 decimal places) to

$$
\begin{aligned}
& \quad 3.924 \;\; (60.4\%) \;\; bound\ states \\
& + \quad 2.234 \;\; (34.4\%) \;\; mixed\ states \\
& + \quad 0.341 \;\; (5.2\%) \;\; scattering\ states \\
& = \quad 6.499
\end{aligned}
$$

One can show that spatially, both electrons stay exponentially localized near their nucleus, but quite remarkably, the above result says that there is no spectral localization. Instead, 39.6 % of the interaction energy is contributed by states in which at least one of the electrons has been promoted all the way up into the continuous spectrum of its atom, past all the infinitely many bound states!

4. What are the electrons doing?

In order to link the somewhat abstract quantum formalism to basic chemical intuition, we have analyzed the structure of the corrector wave function for a pair of hydrogen atoms. In particular, we have investigated in which regions of two-body configuration space the probability of finding the electrons is enhanced as compared to the non-interacting system. The main mathematical tool which allows one to do this are maximum principles for elliptic partial differential equations. One of our results is the following:

Theorem 3 [FG06]
If in a system of two hydrogen atoms the angle of one electron with the molecular axis equals θ, then in the limit of large separation the most likely angle of the other electron is

$$
\phi = \begin{cases} -\arctan(\frac{1}{2}\tan\theta), & \theta \in [0, \frac{\pi}{2}], \\ -\arctan(\frac{1}{2}\tan\theta) + \pi, & \theta \in [\frac{\pi}{2}, \pi]. \end{cases}
$$

For example, for $\theta = 45^o$, ϕ seeks value $\arctan(\frac{1}{2}) = 26.565...^o$:
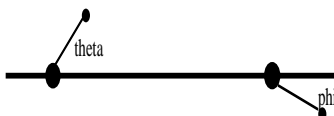
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Sparse Grids for Schrödinger-type equations
Michael Griebel

For the electronic Schrödinger equation, Yserentant has recently shown that solution wavefunctions possess bounded mixed weak derivatives. This makes it worthwhile to explore the benefit of sparse grid or hyperbolic cross techniques to solve equations of this type.

Sparse grid methods exhibit a substantially lower complexity with respect to the problem dimension than conventional discretization techniques. Furthermore there exists a dimension-adaptive sparse grid variant which adaptively determines important problem dimensions and thus further reduces the dependence of the complexity from the dimension of the problem under consideration.

We consider the use of sparse grids for Schrödinger type equations and investigate possible applications.

Vibrational Levels Associated with Hydrogen Bonds
Alain Joye
(joint work with G. Hagedorn)

The time–independent Born–Oppenheimer approximation [1] allows one to compute the vibrational levels of a molecule by taking advantage of the large masses of the nuclei with respect to that of the electrons. Consequently, an approximation of the ground state energy surface near a non-degenerate minimum is sufficient to get the low-lying vibrational levels as perturbed levels of the corresponding harmonic oscillator.

More precisely, if the configuration space of the nuclei is $\mathbb{R}^d$, and if ϵ^{-4} denotes the ratio mass of the nuclei /mass of the electron, there exists a molecular level $\mathcal{E}(\epsilon)$ which satisfies, for ϵ small enough,

$$(1) \qquad \mathcal{E}(\epsilon) = E_0 + \epsilon^2(n_1\omega_1 + \cdots \ldots n_d\omega_d) + O(\epsilon^4),$$

where E_0 is the minimum of the ground state energy surface, $n_j \in \mathbb{N}$ and $\omega_j > 0$, for $j = 1, \cdots, d$, characterize the harmonic d-dimensional approximation. See the recent review [4] for more details and results.

While this procedure is sufficient and quite successful in many cases, even for realistic values of ϵ, it cannot directly be applied to describe the phenomenon of Hydrogen bonding. Indeed, in a molecule which contains a Hydrogen atom participating in such bonds, the interaction energy of the Hydrogen bond is experimentally lower than that between the other atoms. Also, the mass of the Hydrogen is an order of magnitude smaller than that of a typical nuclei, for example, Carbon. Finally, the experimental data concerning the vibrational spectrum of symmetric tri-atomic molecules with a Hydrogen bond display significant deviations from the approximate harmonic spectrum (1). See [2] for an account of these properties.

We propose in [3] an alternative to the Born–Oppenheimer approximation that is specifically designed to describe molecules with symmetrical Hydrogen bonds. In our approach, the masses of the Hydrogen nuclei scale like ϵ^{-3} whereas those of the heavier nuclei scale like ϵ^{-4}. While the parameter ϵ will eventually tend to zero for our mathematical results to hold, when $\epsilon \simeq 0.082$, which corresponds to the mass of the Carbon atom, the mass of the Hydrogen is approximately equal to $1.015\epsilon^{-3}$, in keeping with our scaling. Also, we employ a specialized form for the electron energy level surface, which takes into account the fact that the harmonic potential acting on the Hydrogen atom is weaker than that acting on the other atoms, by a factor ϵ. Consequently, an-harmonic effects play a role in the leading order calculations of vibrational levels, as $\epsilon \to 0$, in the following sense.

Within our approach, we prove the existence of a normal form Hamiltonian H_{NF}, distinct from the harmonic oscillator and independent of ϵ, such that, for ϵ small enough, there exists a molecular level $\mathcal{E}(\epsilon)$ which satisfies

$$(2) \qquad \mathcal{E}(\epsilon) = E_0 + \epsilon^2\mathcal{E}_2 + O(\epsilon^{2+\xi}),$$

for some $\xi > 0$, where $\mathcal{E}_2$ is an element of the spectrum of H_{NF}.

Our analysis is motivated by an examination of symmetric bi-halide ions, such as FHF- or ClHCl-, and we work under the simplifying hypothesis that bending of the molecule is absent. However, we develop a general theory which is suitable for the description of rigid linear asymmetric tri-atomic molecules as well.

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Information measures for the relativistic hydrogen atom

JACOB KATRIEL

(joint work with K. D. Sen)

The characterization of inherent quantum mechanical uncertainties and information measures has become a rich field of study with direct relevance to the emerging technologies associated with the paradigm of quantum computation. The present talk reviews the application of commonly used information measures, notably the Shannon information entropy [1] $S_r = -\int \rho(\mathbf{r}) \ln \rho(\mathbf{r}) \, d\mathbf{r}$, the Fisher information measure [2] $I_r = \int \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} \, d\mathbf{r}$, the residual position entropy [3] $S_r^{R/NR} = \int_0^\infty 4\pi r^2 \rho_R(r) \log\left(\frac{\rho_R(r)}{\rho_{NR}(r)}\right) \, d\mathbf{r}$, the average position density [4] $<\rho> = \int_0^\infty 4\pi r^2 \left(\rho(r)\right)^2 \, d\mathbf{r}$, and the average measure of relative distance [5] $\tilde{S}_r = \int_0^\infty 4\pi r^2 \left(\rho_R(r) - \rho_{NR}(r)\right) \log\left(\frac{\rho_R(r)}{\rho_{NR}(r)}\right) \, d\mathbf{r}$, as well as the corresponding momentum space quantities, to the ground state of the relativistic hydrogen-like atoms. Here, $\rho(r)$ is the position density, R stands for relativistic, NR for non-relativistic. Spherical symmetry is assumed.

As an illustration we present the relativistic Shannon position entropy $S_r^R = \log\left(\frac{\pi \Gamma(2\gamma+1)}{2Z^3}\right) + (2\gamma+1) - 2(\gamma-1)\Psi(2\gamma+1)$, where $\Psi(z)$ is the Digamma function. In the nonrelativistic limit $\gamma \to 1$ this expression reduces to $S_r^{NR} = 3 + \log(\pi) - 3\log(Z)$. The relativistic correction can be expanded as $S_r^R - S_r^{NR} \approx -(\alpha Z)^2 + \left(\frac{3}{8} - \frac{\pi^2}{12}\right)(\alpha Z)^4 + \cdots$.

We point out and illustrate a well-established but largely ignored difficulty associated with the common formulation of the uncertainty principle in terms of position and momentum variances, when applied to the radial coordinate in a spherically symmetric system. This difficulty arises as a consequence of the fact that the radial momentum operator is not self-adjoint [6]. Its most direct manifestation involves the fact that the position space expectation value of the commonly used "radial momentum operator" [7] $\hat{p}_r = -i\left(\frac{\partial}{\partial r} + \frac{1}{r}\right)$ vanishes, whereas the momentum space expectation value of the radial momentum p in the ground state of the hydrogen-like atoms is given by the non-zero expression $\frac{8Z}{3\pi}$.

In the coordinate representation *all* the information measures considered allowed analytic evaluation of the integrals involved. This has not been the case for the corresponding momentum space quantities, that required numerical integration. What we find particularly puzzling is the fact that for the ground state

of the relativistic hydrogen atom the closed analytic expression for the position-space expectation value of the Laplacian $< \Psi_D | - \nabla^2 | \Psi_D > = \frac{2-\gamma}{\gamma(2\gamma-1)} Z^2$, where $\gamma = \sqrt{1 - (\alpha Z)^2}$, agrees, as should be expected, with the numerically evaluated average over p^2 in momentum space, and still we failed to evaluate the latter analytically.

Several relativistic information measures exhibit singularities at particular nuclear charges, notably $Z = \frac{\sqrt{3}}{2\alpha} \approx 118.68$ and $Z = \frac{\sqrt{15}}{4\alpha} \approx 132.68$, whose significance remains to be elucidated.

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Some thoughts on the numerical solution of the eigenvalue problem
RICHARD B. LEHOUCQ

We consider the electronic structure generalized eigenvalue problem

$$\mathbf{H U}_\ell = \mathbf{M U}_\ell \Lambda_\ell, \quad \left(\mathbf{H}, \mathbf{M} \in \mathbb{R}^{n \times n}, \quad \mathbf{U}_\ell \in \mathbb{R}^{n \times \ell}, \quad \Lambda_\ell \in \mathbb{R}^{\ell \times \ell} \right)$$

that arises during an SCF iteration where $\mathbf{H}$ is Hermitian, $\mathbf{M}$ is symmetric positive semi-definite. We order the eigenvalues $\lambda_1 \leq \lambda_2 \leq \cdots \leq \lambda_n$ located on the diagonal of Λ_ℓ. Electronic structure calculations typically require $25\% - 50\%$ of the leftmost eigenpairs $n = 1,000 - 10,000$ for Gaussians; n increases up to $100,000$ for plane wave calculations, and $1\% - 5\%$ of the eigenpairs are of interest.

Two broad classes of eigensolvers are dense methods that consume $O(n^2)$ storage and $O(n^3)$ computation. LAPACK is the archetype. The second class are sparse methods where $\mathbf{H}$ only needs to be known via a matrix-vector multiplication. Subspace iteration, inverse iteration, Davidson and Lanczos methods are the archetypes. Cost of orthogonality and, to a lesser extent, lack of robustness are the difficulties with these approaches.

My presentation discusses some alternatives that need to be considered. These include

- computing the quantity of interest, or the functional, for example, the density;
- avoiding the SCF iteration and computing the ground state directly;

- Linear scaling techniques [4] (that perhaps exploit mulitlevel preconditioners)
- Domain decomposition approaches [1] that avoid the onerous cost of orthogonality

For example, computing an approximation to the density (matrix)

$$\mathbf{U}_\ell(\mathbf{U}_\ell^T\mathbf{M}\mathbf{U}_\ell)^{-1}\mathbf{U}_\ell^T \in \mathbb{R}^{n\times n}, \quad \mathbf{U}_\ell \in \mathbb{R}^{n\times \ell}$$

directly. Such a technique avoids computing the eigenvectors and instead, computes the quantity of interest, namely an *approximation* to the matrix function directly. Consider subspace approximations to matrix functions. For example, generate a subspace via the Lanczos iteration as depicted in Figure 1. The compu-
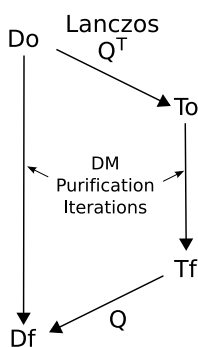
FIGURE 1. Density matrix methods in a Lanczos subspace. The Lanczos matrices $\mathbf{Q}$ and $\mathbf{Q}^T$ represent interpolation and restriction to a subspace.

tation is $O(n^3)$ but has smaller prefactor. A convergence theory subspace density matrix methods is possible via a relationship with subspace iteration.

Another example is an approach for avoiding the SCF iteration via a Carr-Parnello (CP) type of approach (see [13] for a discussion) applied to computing the electronic ground state. We now pose CP as an abstract minimization problem. Let $\mathbf{N}\ddot{\mathbf{x}} = \mathbf{x}(\frac{\mathbf{x}^T\mathbf{H}\mathbf{x}}{\mathbf{x}^T\mathbf{M}\mathbf{x}}) - \mathbf{H}\mathbf{x} \equiv \mathbf{f}$, where $\mathbf{N} \in \mathbb{R}^{n\times n}$ is a symmetric positive definite matrix. Find $\mathbf{u} \in \mathbb{R}^n$ so $\min_{\mathbf{u}} \|\mathbf{u} - \mathbf{N}^{-1}\mathbf{f}\|_{\mathbf{N}}$ subject to $\frac{1}{2}\dot{\mathbf{x}}^T\mathbf{N}\dot{\mathbf{x}} = \frac{\nu}{2}$. This is nothing more than Gauss' principal of least constraint (GPLC) subject to a non-holonomic constraint. The optimality system is $\mathbf{N}\ddot{\mathbf{x}} = \mathbf{f} - \mathbf{N}\dot{\mathbf{x}}(\frac{\dot{\mathbf{x}}^T\mathbf{f}}{\nu}) = (\mathbf{I} - \frac{1}{\nu}\mathbf{N}\dot{\mathbf{x}}\dot{\mathbf{x}}^T)\mathbf{f}$. I remark that the fictitious mass matrix $\mathbf{N}$ represents a change of coordinate or (preconditioning). This view may help to justify rigourously the many CP choices (and derive others) that are physics based.

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On the Computation of Excited States with MCSCF Methods

MATHIEU LEWIN

(joint work with E. Cancès and H. Galicher)

In Quantum Chemistry, the multiconfiguration (MCSCF) method is the main tool for the computation of excited states of quantum electrons in a molecule. We report here results which have been obtained in [4] and in a collaboration [1] with Éric Cancès and Hervé Galicher. An extended review can be found in [5]. Let us consider a molecule containing M nuclei and N non-relativistic electrons. The nuclei are treated as pointwise particles, of charges Z_m and located at positions $R_m \in \mathbb{R}^3$, $m = 1...M$. The state of the N electrons is an normalized antisymmetric wavefunction $\Psi \in \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3)$ with associated energy $\mathcal{E}(\Psi) = \langle \Psi, H_N \Psi \rangle$ where H_N is the N-body quantum Hamiltonian:

$$H_N = \sum_{i=1}^{N} \left(-\frac{\Delta_{x_i}}{2} + V(x_i) \right) + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|}, \qquad V(x) = \sum_{m=1}^{M} \frac{-Z_m}{|x - R_m|}.$$

When $N - 1 < Z := \sum_{m=1}^{M} Z_m$, the spectrum of H_N takes the form $\sigma(H_N) = \{\lambda_0 \leq \lambda_1 \leq \cdots\} \cup [\Sigma, \infty)$ where λ_i is a sequence of eigenvalues of finite multiplicity converging to the bottom of the essential spectrum Σ. We denote by $\bar{\Psi}_i$ an

associated sequence of eigenfunctions, $H_N \bar{\Psi}_i = \lambda_i \bar{\Psi}_i$.

In the MCSCF method, one chooses a number of orbitals $K \geq N$ and restricts H_N to the class of N-body wavefunctions having the special form

$$\Psi_{(c,\Phi)} = \sum_{1 \leq i_1 < \cdots < i_N \leq K} c_{i_1,\ldots,i_N} \varphi_{i_1} \wedge \cdots \wedge \varphi_{i_N}$$

where $\wedge$ is the usual antisymmetric tensor product, $c = (c_{i_1,\ldots,i_N}) \in S^{\binom{K}{N}-1}$ and $\Phi = (\varphi_1, \ldots, \varphi_K) \in (H^1(\mathbb{R}^3))^K$, $\int_{\mathbb{R}^3} \varphi_j \varphi_j = \delta_{ij}$. The associated energy

$$\mathcal{E}_N^K(c,\Phi) := \left\langle \Psi_{(c,\Phi)}, H_N \Psi_{(c,\Phi)} \right\rangle_{\bigwedge_1^N L^2(\mathbb{R}^3)} = \left\langle c, H_\Phi c \right\rangle_{\mathbb{R}^{\binom{K}{N}}}$$

is quadratic with respect to c but non quadratic with respect to the orbitals φ_i's. In the previous formula, we have introduced the matrix H_Φ of the Hamiltonian H_N when it is restricted to the space $V_\Phi := \mathrm{Span}(\varphi_{i_1} \wedge \cdots \wedge \varphi_{i_N})$. Any stationary point (c,Φ) of $\mathcal{E}_N^K$ on the manifold

$$\mathcal{M}_N^K := \left\{ (c, \Phi \in S^{\binom{K}{N}-1} \times (H^1(\mathbb{R}^3))^K, \int_{\mathbb{R}^3} \varphi_i \varphi_j = \delta_{ij} \right\}$$

is the solution of a complicated system of K nonlinear coupled elliptic partial differential equations for the orbitals φ_i's together with a simple eigenvalue equation, $H_\Phi c = \beta c$, for the configuration coefficients c.

The existence of a minimizer for $\mathcal{E}_N^K$ on $\mathcal{M}_N^K$ and the convergence of the associated N-body wavefunction towards a ground state $\bar{\Psi}_0$ of the Hamiltonian as $K \to \infty$, was proven by Friesecke in [2]. A different proof was given in [4], allowing to treat more practical methods in which not all the Slater determinants are considered. In the special cases $K = N$ (Hartree-Fock model) and $K = N + 2$, proofs were already given respectively by Lieb and Simon [6] and Le Bris [3].

For excited states, the situation is more involved: the nonlinear energy $\mathcal{E}_K^N$ has a lot of critical points and it was observed that not all correspond to physical states. Let us denote by $\mu_d^K(\Phi)$, $d = 0 \ldots \binom{K}{N} - 1$ the eigenvalues of the Hamiltonian matrix H_Φ in a fixed orbitals basis $\Phi = (\varphi_1, \ldots, \varphi_K)$. In Quantum Chemistry (see, e.g., [8]), a dth excited state is usually defined as a pair (c,Φ) such that c is a $(d+1)$th eigenvector of H_Φ and Φ minimizes $\mu_d^K(\Phi)$, i.e. it is a solution of:

(1) $$\mu_d^K := \inf_\Phi \mu_d^K(\Phi).$$

However (1) is a minimization of an eigenvalue of a matrix depending of a parameter Φ, a very ill-posed variational method in general: on the one hand in case of degeneracy it could be that the energy has no critical point at the so-defined level (see examples in [4, 1, 5]). On the other hand, there is no general numerical method for eigenvalue minimization except in very special cases.

In [4], an alternative definition of the dth excited state energy was proposed. It is based on a complicated nonlinear min-max variational problem which does not suffer from the above theoretical drawback. More precisely, the dth MCSCF excited state energy was defined as: $\lambda_d^K = \inf_{\substack{f \in \mathcal{C}^0(S^d, \mathcal{M}_N^K) \\ f(-x) = (-) \cdot f(x)}} \sup_{t \in S^d} \mathcal{E}_N^K(f(t))$

where $(-) \cdot (c,\Phi) = (-c,\Phi)$ and the existence of stationary points with a Morse

index at most d at the levels λ_d^K was proved. Additionally it holds $\lambda_d^K \geq \lambda_d$ and $\lim_{K \to \infty} \lambda_d^K = \lambda_d$.

For the first excited state, the above formula can be simplified: one obtains that λ_1^K equals the mountain pass energy on the manifold $\mathcal{M}_N^K$, between two ground states having opposite configuration coefficients. Denoting by (c_0, Φ_0) a minimizer of $\mathcal{E}_N^K$ on $\mathcal{M}_N^K$, the formula reads

$$(2) \qquad \lambda_1^K := \inf_{\substack{\gamma \in \mathcal{C}^0([0;1], \mathcal{M}_N^K) \\ \gamma(0)=(c_0,\Phi_0),\ \gamma(1)=(-c_0,\Phi_0)}} \sup_{t \in [0;1]} \mathcal{E}_N^K(\gamma(t)).$$

This definition is somewhat natural since also for the linear case, one can obtain the first excited state $\bar{\Psi}_1$ as a mountain pass point between $\bar{\Psi}_0$ and $-\bar{\Psi}_0$. Furthermore, it suggests a new algorithm for the computation of the first excited state which was described and tested in [1]: after having found an MCSCF ground state, one solves the mountain pass problem by deforming discretized paths on the manifold until convergence of the highest point along the path.

This algorithm was tested in [1] on the simplest case of two-electron systems. For the molecule H_2, the first singlet excited state was searched in the whole space without imposing any symmetry (for the Schrödinger case, it is known that the ground and first excited states have a certain symmetry). As already predicted in [7], we found that the definition (1) is *not* valid in this case: the optimal c_1 is the *first* eigenvector of the Hamiltonian matrix H_{Φ_1} and not the second. Additionally, we observed a symmetry breaking phenomenon: although the nonlinear ground state automatically has the same symmetry as the Schrödinger solution, this is not valid for the first nonlinear excited state which has no particular symmetry, in contrary to the true solution. Furthermore the following inequality was observed $\lambda_1^K < \mu_1^K$ and the solution of the variational problem (1) is in this case an unphysical (spurious) solution of the MCSCF equations.

All this shows that computing excited states with MCSCF methods is not an easy task and that the definition (2) could be a useful tool in particular when the simpler definition (1) fails.

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Tutorial on coherent states

ELLIOTT H. LIEB

This was a spontaneous, unplanned talk of an hour about the definition and use of coherent states to estimate properties of the ground states of atoms and molecules. The material was largely from my review article [1, pages 621-622]. There was also mention of 'upper' and 'lower' symbols to to get upper and lower bounds to ground state energies [2], [3] , [4] .

The reason this material was presented was that it was felt, in discussions, that there were some chemists and mathematicians who were unfamiliar with this helpful mathematical device and who might want to hear something about it.

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Variational approximations in quantum molecular dynamics

CHRISTIAN LUBICH

The talk considered models that are intermediate between the full molecular Schrödinger equation and classical molecular dynamics described by Newtonian equations of motion for the nuclei. A large variety of such models have been proposed in the literature, but practically all of them rely on the *Dirac–Frenkel variational approximation principle*, which in an abstract form can be stated as follows: given an approximation manifold $\mathcal{M}$, an approximation $u(t) \in \mathcal{M}$ to a solution of the Schrödinger equation $i\hbar\dot{\psi} = H\psi$ is determined by the condition that at all times t, the defect is orthogonal to the tangent space at the current approximation value: $\langle i\hbar\dot{u} - Hu, \delta u \rangle = 0$ for all $\delta u \in T_u\mathcal{M}$. The approximation is thus determined by the choice of the approximation manifold: the time-dependent Born-Oppenheimer approximation, the (multiconfiguration) time-dependent Hartree method, and Gaussian wavepacket dynamics are widely known examples.

The talk discussed the different interpretations of the Dirac-Frenkel variational approximation: provided that the tangent spaces are complex linear, it can be

viewed as both an orthogonal and a symplectic projection. The latter interpretation implies that the equations of motion retain a Hamiltonian structure, and a Poisson structure in local coordinates. The interpretation as an orthogonal projection permits to derive approximation results: an *a posteriori* error bound and, under suitable assumptions satisfied for example in the multiconfiguration Hartree method and in Gaussian wavepacket dynamics, a quasi-optimality result which bounds the approximation error of the variational approximation in terms of the best-approximation error of the wave function on the approximation manifold.

The second part of the talk discussed numerical integration methods for the equations of motion resulting from variational approximations. After a digression into splitting methods for the linear Schrödinger equation, variational splitting methods were introduced as a formal analogue for the treatment of the variational equations of motion. It turns out that variational splitting can be put to good use in various situations: in the multiconfiguration time-dependent Hartree method it leads to explicit integrators without step size restriction by the space discretization, and with approximation properties that parallel those of splitting methods in the linear case. Particularly nice properties of variational splitting are obtained for Gaussian wavepacket dynamics: there, the substeps can be solved analytically and explicitly, leading to a method for which the numerical flow is a Poisson map, which preserves the norm and preserves linear and angular momentum in the case of translational or rotational invariance, and has no drift in the energy over exponentially long times in the time step. In the semi-classical limit the variational splitting integrator turns into the Verlet scheme, which is the standard integration method in classical molecular dynamics.

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Reduced Basis Approach for Rapid Electronic Structure Calculations
George S. H. Pau
(joint work with E. Cancès, C. Le Bris, Y. Maday, A. T. Patera)

1. Introduction

Computational quantum chemistry problems generally require the repetitive determination of certain selected output of interest, s — such as the ground state energies of the system and the forces exerted on the nuclei — as functions of input parameter $\mu \in \mathcal{D}$ — such as nuclei positions and dimensions of the simulation cell of a crystalline system — where $\mathcal{D} \in \mathcal{R}^P$ is the parameter space in which our input μ varies. These outputs, $s(\mu)$ are functionals of a field variable $u(\mu)$ — such as the molecular or crystalline orbitals, and the electron density — which satisfies the μ-parametrized partial differential equations, derived from the Hartree Fock or the Density Functional Theory models. In practice, the solution $u(\mu)$ is obtained though a high-dimensional Galerkin approximation (of dimension $\mathcal{N}$), such as the planewave method. Clearly, solving the resulting discrete algebraic system is computationally intensive, and in some cases, impractical in any realistic real-time, many query context.

The above abstraction of the problems into one of input-output relations highlights several computational opportunities, which can be successfully exploited by the reduced-basis techniques to obtain rapid and reliable solutions. First, we exploit the parametric manifold arguments to project the solution into a significantly lower-dimensional system (of dimension N, with $N \leq \mathcal{N}$) to obtain the reduced basis approximant to the solution $u(\mu)$. Availability of *a posteriori* error estimate then qualifies the accuracy of the approximation and provides a guide to increased solution accuracy by simply increasing the richness of the reduced basis space. Second, we can, in most cases, decompose the differential operators into sum of Q products of parameter-*dependent* functions and parameter-*independent* operators; reduced basis procedures then exploit this underlying affine parametric structure to design effective *offline-online* computational procedures which willingly accept greatly increased initial preprocessing — offline — expense in exchange for greatly reduced marginal — online — "in service" cost.

The reduced-basis approach and in particular associated *a posteriori* error estimation procedures have been successfully developed for (*i*) linear elliptic and parabolic PDEs that are affine in the parameter [5, 6, 7, 9, 12] ; and (*ii*) elliptic PDEs that are at most quadratically nonlinear in the first argument [8, 10, 11]. For these problems, the operation count for the online stage — in which, given a new parameter value, we calculate the reduced-basis output and associated error bound — depends only on N (typically small) and Q, but it is *independent* of $\mathcal{N}$. The essential components of the reduced basis method are

(1) *Reduced basis approximation (N ≪ $\mathcal{N}$)*: rapidly convergent global reduced basis approximation spaces are generated by Galerkin projection onto a

space W_N spanned by solutions of the governing partial differential equations at N judiciously chosen samples in parameter space. Here, W_N is simply an approximation of the parametric manifold.

(2) *A posteriori error estimation*: the dual norms of the primal and adjoint error residual equations, and an approximate stability constant, are used to provide inexpensive yet sharp bounds for the errors in the outputs of interest.

(3) *Offline/online decompositions*: exploit affine nature (with respect to the input parameter μ) of the linear and bilinear forms — or render them affine using empirical interpolation techniques [1, 4] — to decouple the generation and projection stages of the approximation process. Since $N \ll \mathcal{N}$, the projection system (although dense) provides significant computational speedups compared to typical methods, such as the planewave method.

(4) *Optimal Sampling Strategies*: exploit the rigorous error estimates produced by the reduced-basis approximation as a guide to pick parameter samples judiciously. Exhaustive parameter explorations can be undertaken — relying on the computational speedups and the accurate predictions — to uncover relevant (significant) parametric dependence of the outputs.

This work entails extending the reduced basis techniques to quantum chemistry problems, particularly electronic structure calculations based on Density Functional Theory models. We shall demonstrate the effectiveness of the techniques in two applications: geometry optimization and band structure calculation.

2. Geometry Optimization

We are interested in the rapid determination of the ground state energy, $\mathcal{E}(\mu)$, of some molecular systems — in [2], we applied the reduced basis techniques to a hydrogen molecular system based on the Hartree Fock model and a crystal structure based on the Density Functional Theory — with possible applications in geometry optimization and multiscale simulations. Here, we will focus on a crystal structure characterized by the parameter μ, particularly those parameters that describe the geometric variation of the simulation cell. Application of the reduced basis techniques to this problem leads to three main issues: (*i*) the parametrizations of the Kohn-Sham equations can be complex, for example due to a set of moving nuclei and periodic boundary conditions; (*ii*) the equations can contain both non-affine terms and also very nasty nonlinear terms, for example the local pseudopotential term and the exchange-correlation term; and (*iii*) the solution sought is not scalar — for each μ, it is a set of orthonormal eigenvectors of some mean-field hamiltonian (which itself depends on μ, but also, self-consistently, on $u(\mu)$).

We effect the parametrization of the equations by mapping the solutions onto a fixed reference domain; positions of nuclei can be parametrized by mapping them onto unique locations in the reference domain. We then render all nonaffine and nonlinear functions affine by using empirical interpolation procedure. Lastly, we introduce the vector reduced-basis space which allows us to exploit the inherent orthogonality properties between, and the common smoothness of the solutions

$u_i(\mu)$, $1 \le i \le n_e$, where n_e is the number of bands. Given a parameter sample $S_N = \{\mu_1, \ldots, \mu_N\}$, we define the associated reduced-basis spaces as

$$\begin{aligned} W_N &= \mathrm{span}\ \{\hat{\mathbf{u}}(\mu_n), 1 \le n \le N\}, \\ &= \mathrm{span}\ \{\hat{\zeta}_n, 1 \le n \le N\}; \end{aligned}$$

where $\hat{\zeta} \equiv (\zeta_1, \ldots, \zeta_{n_e})$ are basis functions obtained after

$$\hat{\mathbf{u}}(\mu_n) \equiv (u_1(\mu_n), \ldots, u_{n_e}(\mu_n)), 1 \le n \le N$$

are aligned and pseudo-orthogonalized [2]; these two preprocessing steps will lead to smaller N and better stability in the resulting discrete system. Then, an approximation of $\hat{\mathbf{u}}$ in W_N is given by $\hat{\mathbf{u}}_N(\mu) = \sum_{n=1}^{N} \psi_n(\mu)\hat{\zeta}_n$. This construction also allows us to only impose the normality constraints on $\hat{\mathbf{u}}_N$; we prove that the orthogonality constraints are increasingly satisfied as error in $\hat{\mathbf{u}}_N$ decreases and it is easily verifiable during computation.

Our preliminary results based on a 1-dimensional periodic problem indicate that the reduced-basis space is rapidly convergent with N and N scales as $n_e + C$, where C is a small integer. In addition, the complexity of the online computation is independent of $\mathcal{N}$. The energy $\mathcal{E}(\mu)$ can also be easily approximated to an accuracy of 10^{-10} with this approach. Progress is currently being made to demonstrate the same with 3-dimensional model with multiple nuclei and more complex parametrization of the unit cell.

3. BAND STRUCTURE CALCULATION

In the second application, we are interested in the rapid determination of $\hat{\mathbf{u}}(\mathbf{k})$, given any $\mathbf{k}$ in the first Brillouin zone (BZ) for a periodic Hamiltonian operator of the form $-\frac{1}{2}\Delta - \mathrm{i}|\mathbf{k}|\nabla + V_{\mathrm{eff}}$; this has potential applications in improving the efficiency of Self-Consistent Field (SCF) algorithms by reducing the costs of evaluating $\hat{\mathbf{u}}(\mathbf{k})$ within each SCF iteration, and in rapid reconstruction of the band structure diagram.

We propose a reduced-basis approach: we construct a reduced basis space spanned by the solutions at N $\mathbf{k}$-points in BZ and our reduced basis approximation of $\hat{\mathbf{u}}(\mathbf{k})$ is a Galerkin projection onto this space; here, an augmented basis space, defined as $W_{N_A} = \mathrm{span}\ \{\zeta_{i,n}, 1 \le i \le n_e, 1 \le n \le N\}$, works better than the vectorized reduced basis space described in previous section. The parametrization of the equations is also considerably simpler compared to previous application; the equation is affine in the parameter space. In addition, V is not dependent on $\mathbf{k}$ and the resulting equation is more akin to a linear eigenproblem. We are also able to construct an efficient asymptotic *a posteriori* error estimation procedure for our approximations, enabling us to control the accuracy of the approximation, and provide an inexpensive guide to efficiently construct an optimal reduced basis space. Let n_k be the number of $\mathbf{k}$ points for which $\hat{\mathbf{u}}(\mathbf{k})$ needs to be approximated accurately. Then, to leading order, the complexity of obtaining the reduced basis approximant $\hat{\mathbf{u}}_N(\mathbf{k})$ is $O(N\mathcal{N}^c + n_k(Nn_e)^3)$ where c reflects the complexity of the solver used to obtain $\hat{\mathbf{u}}(\mathbf{k})$; this can be compared to $O(n_k\mathcal{N}^c)$ if $\hat{\mathbf{u}}$ are computed

at all n_k points. We conclude that the reduced basis approach will be competitive with the existing techniques, for example the special k-points technique, if $N \ll n_k$ and $Nn_e \ll \mathcal{N}$.

Our results based on a 3-dimensional empirical pseudopotential model for Si [3] is rapidly convergent and our error estimate is a good surrogate to the actual error. The number of basis functions also increases linearly with n_e. With $n_e = 7$, we require only 119 basis functions.

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One-electron reduced density matrix functional theory -functionals, ionization potentials, and response properties
Katarzyna Pernal

Density matrix functional theory (DMFT) offers an attractive alternative to the DFT (density functional theory) formalism. By employing the one-particle reduced density matrix (1-matrix) as the main variable, one avoids any references to the fictitious non-interacting state (the explicit expression in terms of the 1-matrix for the kinetic energy functional is known) that constitutes a conceptually weak aspect of practical implementations of DFT.

The main properties of the 1-matrix functionals and the main issues concerning the related variational equations will be briefly discussed. Then a recent progress in the development of new 1-matrix functionals aimed at reproducing accurate electronic energy for closed-shell molecules will be presented.

Within the density matrix functional theory one is not limited to computing approximate ground-state energy. The connection between the variational equations and the extended Koopmans' theorem equations offers a simple way of computing the ionization potentials without obtaining the energy for the ionized species. This method, together with the results for the recently proposed functionals, will be presented in the second part of the talk. Finally an algorithm proposed for computing second-order response properties that originates from perturbed variational equations for the 1-matrix will be discussed.

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Free energy profiles in Molecular Dynamics
Mathias Rousset
(joint work with G. Stoltz, T. Lelièvre)

Consider a classical dynamical system in $\mathbb{R}^{3N}$ with an interaction potential V, and a selected degree of freedom (called the reaction coordinate) $\xi : \mathbb{R}^{3N} \to \mathbb{R}$, usually exhibiting a typical evolution of the system at a slow time scale. The free energy is a function of all different values z of ξ. It is defined through the normalisation of the Boltzmann distribution of configurations restricted to the fixed value z of their reaction coordinate. The free energy gives the Boltzmann weights of the equilibrium distribution of the reaction coordinate.

In many applications, the quantity of interest is the free energy difference between an initial and a final state (characterized by two different values of the parameter z). These differences characterize the relative stabilities of several species, as well as their transition kinetics. Classical techniques to this end fall within three main classes. The first one, dating back to Kirkwood [11], is thermodynamic integration, which computes for each value of z the derivative of the free energy using some finite temperature sampling of a constrained dynamics (like constrained Hamiltonian dynamics (see [1]) or Brownian dynamics (see [5, 3])). Some finite difference of free energy can also be considered, which is essentially the free energy perturbation method, was introduced by Zwanzig [24]. The second and most recent class of methods uses dynamics arising from a switching at a finite rate. This can be done using nonequilibrium dynamics with a suitable exponential reweighting in an ensemble of realizations of these dynamics, as introduced by Jarzynski in [9]. Notice that the thermodynamic integration and free energy perturbation methods can be seen respectively as the limits of infinitely slow and fast switching of nonequilibrium dynamics. Instead of being imposed *a priori*, this switching may also arise as the result of a bias of the dynamics which is as close as possible to the target free energy to be computed, as in the celebrated umbrella sampling [22]. In a more subtle fashion, this bias can be learned using adaptive techniques, for example [4, 7]. In this case, the dynamics is progressively forced to leave regions where the sampling of the reaction coordinate has been completed.

It is still a matter of debate which method is the most efficient. While some results show that out of equilibrium methods can be competitive in some situations [6], other studies disagree [15]. Generally speaking, methods using a bias seem to be more relevant that methods using constraints, but some mathematical justifcation of is lacking.

We propose in our list of papers, some mathematical analysis and refinements of these methods.

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Quantum control: theoretical, numerical and experimental results

GABRIEL TURINICI

Controlling the evolution of molecular systems at quantum level has been envisioned from the very beginnings of the laser technology. However, approaches based on designing laser pulses resulting from intuition alone did not succeed in general situations due to the very complex interactions that are at work between the laser and the molecules to be controlled, which results e.g., in the redistribution of the incoming laser energy to the whole molecule which prevents it from acting accordingly to the intuition. Even if this circumstance initially slowed down investigations in this area, the realization that this inconvenient can be recast and attacked with the tools of (optimal) control theory [8] greatly contributed to the first positive experimental results [2, 11, 18, 5, 4, 7, 9].

Historically, the first applications that were envisioned were the manipulation of chemical bonds (e.g., selective dissociation) or isotopic separation. Then, further

poly-atomic molecules were considered in strong fields, High Harmonic Generation) [6] was introduced and more techniques are also explored to enhance detection in the atmosphere. Beyond chemistry, applications are also important for the emerging generations of laser sources [3].

The purpose of this contribution is to explore the contributions coming from mathematicians and that are useful in quantum chemistry framework. We will explore :

- the controllability which speaks to the possibility to control a quantum system to a given target state. Although geometric control is already giving an abstract answer, more intuitive criterions are also available [15, 16, 1, 12, 13]. Beyond the one-molecule setting, recent works have shown that surprising recent results [17] show that a single laser source may be able to independently control a finite number of uncoupled quantum systems

- the possibility to numerically find a solution to the control problem is given by the introduction of specific iterative algorithms, among which the monotonic algorithm. The monotonic algorithms have the very convenient property of improving at each iteration the quality of the solution. These algorithms are shown to be equivalent to Lyapunov formulations [14] and also represent an alternative view where one asks for providing at each instant a good solution candidate.

- the possibility to gain information on the system at hand, especially in the situations when the control can be found without such previous data on the system. We investigated in recent works [10] what are the information / measurements that can lead to an unique identification of the characteristics of the system and of the coupling operators : the problem is thus restated as an uniqueness of the solution of an inverse problem.

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Parareal in time control for quantum systems

JULIEN SALOMON

(joint work with Y. Maday, G. Turinici)

Following recent encouraging experimental results in quantum control, numerical simulations have known significant improvements through the introduction of efficient optimization algorithms. Yet, the computational cost still prevents using these procedures for high-dimensional systems often present in quantum chemistry. Using the parareal in time framework, we present here a time parallelization of these schemes which allows to reduce significantly their computational cost while still finding convenient controls.

Minimisation principles for density-functional theory: Relativity and time-dependence

TROND SAUE

Density-functional theory treats electron correlation efficiently at low computational cost and has therefore become the dominant method in the field of theoretical chemistry [1, 2]. In my talk I would like to adress, if time allows, two issues concerning DFT that calls for the expertise of mathematicians, namely i) the relativistic extension of the Hohenberg-Kohn theorem that establishes a one-to-one

correspondence between the ground-state electron density and energy, and ii) the quasienergy formalism [3, 4, 5] as an alternative to the Runge-Gross theorem [6] for time-dependent DFT. Both issues requires the demonstration of the existence of a minimsation principle. I will focus on the first issue.

The importance of relativity in chemistry is now widely established. 4-component relativistic molecular calculations, starting from the Dirac equation, have nowadays reached a stage of maturity that allows such calculations to be carried out on a routine basis and with a wide choice of methods such as Hartree-Fock (HF), Density Functional Theory (DFT), Möller-Plesset perturbation theory as well as Configuration Interaction (CI) and Coupled Cluster (CC) expansions. A rigorous justification of 4-component relativistic DFT was provided by Rajagopal and Calloway [7] by the relativistic extension of the Hohenberg-Kohn theorem in the framework of full QED. However, this is not the framework in which conventional 4-component relativistic calculations are carried out. Moreover, the existence of the required minimisation principle is only postulated, not proven, in the framework of full-fledged QED. I will argue that a minimisation principle can be obtained by inclusion of vacuum polarisation in 4-component relativistic theory.

It is known that the Dirac equation is not exact since it does not predict the splitting between the $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ states in hydrogen observed by Willis E. Lamb and R. C. Retherford in 1947. The Lamb shift is due to vacuum polarization and the self-energy of the electron. The two effects have opposite sign, with the latter dominating. Recently there has been some interest in assessing the effect of QED corrections in chemistry. For the $ns-$levels of heavier elements ($Z > 50$), the QED effects have been found to cancel about -1% of the relativistic effects obtain by conventional 4-component calculations [8, 9, 10].

At this point one may ask what has to be added to conventional 4-component relativistic calculations in order to make them QED calculations. In conventional calculations external fields are added as parameters whereas in QED particles and fields fully interact. External fields are furthermore quantized. Finally, the fully relativistic two-electron interaction is usually truncated to the Coulomb term only. Certainly the QED corrections can be added perturbatively by evaluating the relevant Feynman diagrams. However, as pointed out by David J. Gross in his 2004 Nobel lecture: *"... the Feynman rules were too successful. They were an immensely useful, picturesque and intuitive way of performing perturbation theory. However, these alluring qualities also convinced many that all was needed from field theories were these rules. They diverted attention from the non-perturbative dynamical issues facing field theory...Today we know that there are many phenomena, especially confinement in QCD, that cannot be understood perturbatively."* It would be immensely useful to formulate QED in a variational manner that can be grafted onto existing quantum chemical methodology.

This paper addresses the variational inclusion of the smaller contribution to the Lamb shift, that is vacuum polarization, and was inspired by the rarely cited work of Chaix and Iracane [11, 12]. I will sketch the minimisation principle that follows upon the variational inclusion of vacuum polarization. A first version of the

theory appeared in [13]. In the following we will use the repeated index summation convention.

Although both formalisms arose in physics, second quantization combined with exponential parametrization has become a powerful tool in the framework of quantum chemistry. The second-quantized Hamiltonian is obtained by introduction of field operators $\Psi(1) = \varphi_p(\mathbf{r}_1) a_p$ In conventional quantum chemical methodology, the second-quantized electronic Hamiltonian is given by

$$
\begin{aligned}
\hat{H} &= \int \Psi^\dagger(1)\hat{h}(1)\Psi(1)d\tau_1 + \frac{1}{2}\int\int \Psi^\dagger(1)\Psi^\dagger(2)\hat{g}(1,2)\Psi(2)\Psi(1)d\tau_1 d\tau_2 \\
&= h_{pq}a_p^\dagger a_q + \frac{1}{4}\mathcal{L}_{pq,rs}a_p^\dagger a_r^\dagger a_s a_q
\end{aligned}
$$

where appears anti-symmetrized two-electron integrals $\mathcal{L}_{pq,rs} = (pq\,|\,rs) - (ps\,|\,rq)$. This Hamiltonian operates in Fock space, spanned by occupation-number vectors which are eigenfunctions of the number operator $\hat{N} = a_p^\dagger a_p$.

Consider next the Hartree-Fock variational ansatz expressed in second-quantization formalism with exponential parametrization. We start from an occupation number vector that maps into a single Slater determinant $|\Phi\rangle = a_1^\dagger a_2^\dagger \ldots a_N^\dagger |0\rangle$ where the vacuum state is defined by $a_i|0\rangle = 0; \quad \forall a_i$.

We next introduce an orbital rotation operator which conserves particle number $\widehat{\kappa} = \kappa_{pq}a_p^\dagger a_q; \quad \kappa_{pq} = -\kappa_{qp}^*; \quad \left[\widehat{\kappa}, \widehat{N}\right] = 0$.

We may now write the Hartree-Fock variational *ansatz* as $\left|\widetilde{\Phi}\right\rangle = \exp\left[-\widehat{\kappa}\right]|\Phi\rangle = \widetilde{a}_1^\dagger \widetilde{a}_2^\dagger \ldots \widetilde{a}_N^\dagger |0\rangle$; $\widetilde{a}_p^\dagger = \exp\left[-\widehat{\kappa}\right]a_p^\dagger \exp\left[\widehat{\kappa}\right]$ The orbital rotation operator induces rotations amongst the orbitals of our 1-particle basis, but the vacuum itself is conserved $\exp\left[-\widehat{\kappa}\right]|0\rangle = |0\rangle$.

A first step towards QED is to introduce a particle-hole formalism by redefining the field operators as $\Psi = \varphi_p^+ b_p + \varphi_p^- d_p^\dagger$ where we have introduced *electron* annihilation operators b_p associated with the positive-energy orbitals φ_p^+ and *positron* creation operators $d_p^\dagger$ describing the creation of positrons whose orbitals are obtained by charge conjugating the associated negative-energy orbitals φ_p^-. This leads to a much more involved Hamiltonian

$$
\hat{H} = h_{pq}^{++}b_p^\dagger b_q + h_{pq}^{+-}b_p^\dagger d_q^\dagger + h_{pq}^{-+}d_p b_q + h_{pq}^{--}d_p d_q^\dagger
$$

$$
+ \frac{1}{4}\mathcal{L}_{pqrs}^{++++}b_p^\dagger b_r^\dagger b_s b_q + \frac{1}{4}\mathcal{L}_{pqrs}^{+-++}b_p^\dagger b_r^\dagger b_s d_q^\dagger + \frac{1}{4}\mathcal{L}_{pqrs}^{+++-}b_p^\dagger b_r^\dagger d_s^\dagger b_q + \frac{1}{4}\mathcal{L}_{pqrs}^{+-+-}b_p^\dagger b_r^\dagger d_s^\dagger d_q^\dagger
$$

$$
+ \frac{1}{4}\mathcal{L}_{pqrs}^{++-+}b_p^\dagger d_r b_s b_q + \frac{1}{4}\mathcal{L}_{pqrs}^{+--+}b_p^\dagger d_r b_s d_q^\dagger + \frac{1}{4}\mathcal{L}_{pqrs}^{++--}b_p^\dagger d_r d_s^\dagger b_q + \frac{1}{4}\mathcal{L}_{pqrs}^{+---}b_p^\dagger d_r d_s^\dagger d_q^\dagger
$$

$$
+ \frac{1}{4}\mathcal{L}_{pqrs}^{-+++}d_p b_r^\dagger b_s b_q + \frac{1}{4}\mathcal{L}_{pqrs}^{--++}d_p b_r^\dagger b_s d_q^\dagger + \frac{1}{4}\mathcal{L}_{pqrs}^{-++-}d_p b_r^\dagger d_s^\dagger b_q + \frac{1}{4}\mathcal{L}_{pqrs}^{--+-}d_p b_r^\dagger d_s^\dagger d_q^\dagger
$$

$$
+ \frac{1}{4}\mathcal{L}_{pqrs}^{-+-+}d_p d_r b_s b_q + \frac{1}{4}\mathcal{L}_{pqrs}^{---+}d_p d_r b_s d_q^\dagger + \frac{1}{4}\mathcal{L}_{pqrs}^{-+--}d_p d_r d_s^\dagger b_q + \frac{1}{4}\mathcal{L}_{pqrs}^{----}d_p d_r d_s^\dagger d_q^\dagger
$$

which couples occupation-number vectors with different particle number, but conserves charge.

Consider now the Hartree-Fock method in this new framework. For bound electronic states we start from an occupation-number vector $|\Phi\rangle = b_1^\dagger b_2^\dagger \ldots b_n^\dagger |0\rangle$ with the vacuum defined as $(b_p |0\rangle = 0, \quad \forall b_p)$ and $(d_p |0\rangle = 0, \quad \forall d_p)$. The variational Hartree-Fock *ansatz* is now given by

$$\left| \widetilde{\Phi} \right\rangle = \exp\left[-\widehat{\kappa}\right] |\Phi\rangle; \quad \widehat{\kappa} = \underbrace{\kappa_{pq}^{++} b_p^\dagger b_q}_{\widehat{\kappa}^{++}} + \underbrace{\kappa_{pq}^{+-} b_p^\dagger d_q^\dagger}_{\widehat{\kappa}^{+-}} + \underbrace{\kappa_{pq}^{-+} d_p b_q}_{\widehat{\kappa}^{-+}} + \underbrace{\kappa_{pq}^{--} d_p d_q}_{\widehat{\kappa}^{--}}$$

Using the unitarity of the orbital rotation operator we may now rewrite the HF *ansatz* as $\left| \widetilde{\Phi} \right\rangle = \widetilde{b}_1^\dagger \widetilde{b}_2^\dagger \ldots \widetilde{b}_n^\dagger \left| \widetilde{0} \right\rangle$ with transformed creation operators

$$\widetilde{b}_p^\dagger = \exp\left[-\widehat{\kappa}\right] b_p^\dagger \exp\left[\widehat{\kappa}\right] = b_q^\dagger U_{qp}; \quad U = \exp\left[-\kappa\right]$$

Note, however, that the vacuum is no longer conserved

$$\left| \widetilde{0} \right\rangle = \exp\left[-\widehat{\kappa}\right] |0\rangle = \left\{ 1 - \kappa_{pq}^{--} d_p d_q - \kappa_{pp}^{--} + O(\kappa^2) \right\} |0\rangle \neq |0\rangle$$

The difference between the modified, dressed vacuum and a chosen reference vacuum corresponds to vacuum polarization.

The present formalism has been implemented in a development version of the DIRAC04 code. However, if we evaluate the expectation value of the QED Hamiltonian with respect to the reference determinant we obtain the standard HF energy expression, but with *all* the negative-energy orbitals included amongst the occupied orbitals, thus leading to an infinite negative energy. In order to avoid working with infinite energies renormalization procedures are introduced in QED. Our formalism will furthermore have to cope with singularties. These questions will be addressed in my presentation.

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Conceptual problems in Density Functional Theory

ANDREAS SAVIN

The topic is not new (cf. [1, 2] and references therein). The electronic structure calculations based upon density functionals are highly successful and widely used. Moreover, the Hohenberg-Kohn theorems and the Kohn-Sham method seem to give them a firm basis. However, several basic issues are not solved, and hamper the progress to achieve high accuracy.

The density functional theory aims to obtain the ground state energy and density by using density functionals which can be rigorously defined. Unfortunately, the exact definition does not give a prescription to be followed in practice: approximations are needed.

No approximations are known to satisfy the following two basic requirements:

- to provide reasonable error estimates,
- to be systematically improvable, in the sense that one knows how to improve approximations for reducing the errors.

Typically, the approximations for density functionals have the form: $F(n) = \int f(n_\downarrow(r), n_\uparrow(r), |\nabla n_\downarrow(r)|, |\nabla n_\uparrow(r)|, ...) d^3 r$, where $n_\downarrow(r)$ and $n_\uparrow(r)$ are the spin-up and spin-down densities, respectively (positive functions in $\mathbb{R}^3$, which integrate to the number of electrons with spin-up and spin-down, respectively). The function f is chosen to yield accurate properties for selected systems, e.g., the energy of the uniform electron gas, and/or to satisfy some know properties, e.g., scaling relationships.

This type of approximation is restrictive, as it does not satisfy a requirement considered fundamental for chemistry, namely to insure that the energy (or a conveniently chosen part of it) is size-consistent. (The concept of size-consistency is related to that of extensivity. It means that if one calculates the energy of the system A and that of the system B separately, $E(A)$ and $E(B)$, respectively, one knows the energy of the composite system of A and B, as long as these two entities do not interact, e.g., at infinite separation; it is $E(A) + E(B)$. It is expected that even an infinitesimal interaction will only change infinitesimally the energy from $E(A) + E(B)$.)

If the approximation given above is used, size-consistency would be guaranteed if the function f were intensive (intensive meaning that its value in r in the domain of space pertaining to system A, Ω_A, is not changed by the presence of the system B). A corresponding statement can be made for the integration over the region of atom B. As the integral in the composite system is the sum over the regions of the individual (sub-)systems, extensivity could be guaranteed.

As the density $n(r) = n_\downarrow(r) + n_\uparrow(r)$ is believed to be intensive, one expects extensivity. However, $n_\uparrow$, and $n_\downarrow$ are not intensive, as it is shown by a simple counterexample: the hydrogen molecule at infinite separation of the nuclei. While a single hydrogen atom (doublet ground state) has a spin-density equal to its density, the spin-density of the molecule (singlet ground state) is zero. Simple counterexamples can be also given for the density itself, when the ground-state of the system A is degenerate, as different states can have different densities, and an infinitesimal interaction with B can select one of the states. This change is not infinitesimal, and depends on the nature of B.

In order to obtain the ground state energy of the system, an Euler-Lagrange equation is used, and the functional derivative of the density functional yields a function in $\mathbb{R}^3$, a potential. However, by the definition of the density functionals, this potential is only defined up to an arbitrary constant which is considered irrelevant, as related to the zero of energy which can be arbitrarily chosen.

However, when two systems are put together, each can have its individual constant, and a supplementary degree of freedom appears which has to be fixed in order to avoid charge transfer between the individual (sub-)systems. The approximations do not take this into account.

It is worth mentioning that such effects can take place within a system, e.g., for the two different spins, or for its different parts (e.g., core and valence).

A further problem is that the Hohenberg-Kohn theorem is not valid in a finite space. In practice, this is not an issue, as long one first defines an approximate functional, and obtains from it a potential. However, if one wants to see how the real potential looks like (or in the optimized effective potential method) this becomes important, as we do not know how to approach systematically the infinite basis set potential.

As an example, it can be shown that with finite basis sets one can find the exact wave function in the given basis set (the full CI wave function) as the solution to the Kohn-Sham problem which is a single Slater determinant in the infinite basis set.

There is, however a way to show us what the approximations should be, by introducing model potentials and model interactions in a model Hamiltonian operator, H_m. A parameter λ can be chosen in a way to have the physical operator for a given value of a parameter, e.g., $\lambda = 1$. In density functional theory, one also chooses to obtain, for another value of the parameter, e.g. $\lambda = 0$, a non-interacting system. For each λ, the energy of the system is given by $E = E_m(\lambda) + C(\lambda)$ where $E_m(\lambda) = \langle H_m(\lambda) \rangle$ is the energy of the model system, and C a correction defined by the equation above. As E is independent of λ, $0 = \partial_\lambda E_m + \partial_\lambda C$ or, in an integral form: $C(0) = \int_0^1 \partial_\lambda H(\lambda) d\lambda$ with $E(1) = E, C(1) = 0$. This procedure, called adiabatic connection in density functional theory, allows us to understand the meaning of the corrections we try to construct with approximations.

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Mathematical aspects of relativistic models

ERIC SÉRÉ

(joint work with J. Dolbeault, M.J. Esteban)

In this talk, we deal with some linear and nonlinear models appearing in relativistic quantum chemistry. In these models, the negative continuous spectrum of the free Dirac operator is the source of important mathematical and physical difficulties.

In the first part, we consider a min-max principle allowing to characterize and compute the eigenvalues of linear Dirac operators with an external potential in the gap of their essential spectrum. This principle was first proposed by Talman [10] in 1986. We present rigorous results on this principle and its generalizations [4, 7, 1, 3]. We describe a related stable algorithm [2] to compute the eigenvalues. This algorithm avoids spurious states.

In the second part, we discuss rigorous results [5, 8, 6] that have been obtained on the Dirac-Fock model [9], which is a nonlinear theory describing the behavior of N interacting electrons in an external electrostatic field. In particular we focus on the problematic definition of the ground state and its nonrelativistic limit.

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The Ground State Energy of Heavy Atoms According to Brown and Ravenhall: Absence of Relativistic Effects in Leading Order

HEINZ SIEDENTOP

(joint work with R. Cassanas)

The energy of heavy atoms has attracted considerable interest in the context of nonrelativistic quantum mechanics. Lieb and Simon [14] proved that the leading behavior of the ground state energy is given by the Thomas-Fermi energy which decreases as $Z^{7/3}$. The leading correction to this behavior, the so called Scott correction was established by Hughes [12, 13] (lower bound), and Siedentop and Weikard [16, 17, 18, 19, 20] (lower and upper bound). In fact even the existence of the $Z^{5/3}$-correction conjectured by Schwinger was proven (Fefferman and Seco [8, 9, 10, 3, 11, 6, 4, 5, 7]). Later these results where extended in various ways, e.g., to ions and molecules.

Nevertheless, from a physical point of view, these considerations are questionable, since large atoms force the innermost electrons on orbits that are close to the nucleus where the electrons move with high speed which requires a relativistic treatment. Our main goal in this paper is to show that the leading energy contribution is unaffected by relativistic effects, i.e., the asymptotic results of Lieb and Simon [14] remain also valid in the relativistic context, whereas the question mark behind the quantitative correctness of the other corrections persists.

Sørensen [15] took a first step in this direction. He considered the Chandrasekhar multi-particle operator and showed that the leading energy behavior is given by the non-relativistic Thomas-Fermi energy in the limit of large Z and large velocity of light c. Nevertheless, a question from the physical point of view remains: Although the Chandrasekhar model is believed to represent some qualitative features of relativistic systems, there is no reason to assume that it should give quantitative correct results. Therefore, to obtain not only qualitatively correct results it is interesting, in fact mandatory, to consider a Hamiltonian which – as the one by Brown and Ravenhall [1] – is derived from QED such that it yields the leading relativistic effects in a quantitave correct manner.

Brown and Ravenhall [1] describe two relativistic electrons interacting with an external potential. The model has an obvious generalization to the N-electron case. The energy in the state ψ is defined as

$$\mathcal{E} : \bigwedge_{\nu=1}^{N} (H^{1/2}(\mathbb{R}^3) \otimes \mathbb{C}^4) \to \mathbb{R}$$

(1)

$$\psi \mapsto (\psi, (\sum_{\nu=1}^{N} (D_{c,Z} - c^2)_\nu + \sum_{1 \leq \mu < \nu \leq N} |\mathbf{x}_\mu - \mathbf{x}_\nu|^{-1})\psi)$$

where $D_{c,Z} := \boldsymbol{\alpha} \cdot \frac{c}{i} \nabla + c^2 \beta - Z |\cdot|^{-1}$ is the Dirac operator of an electron in the field of a nucleus of charge Z. As usual, the four matrices $\alpha_1, ..., \alpha_3$ and β are the four Dirac matrices in standard representation. We are interested in the restriction $\mathcal{E}$ of this functional onto $\mathfrak{Q}_N := \bigwedge_{\nu=1}^N (H^{1/2}(\mathbb{R}^3) \otimes \mathbb{C}^4) \cap \mathfrak{H}_N$ where

$$(2) \qquad \mathfrak{H}_N := \bigwedge_{\nu=1}^N \mathfrak{H};$$

the underlying one-particle Hilbert space is

$$(3) \qquad \mathfrak{H} := [\chi_{(0,\infty)}(D_{c,0})](L^2(\mathbb{R}^3) \otimes \mathbb{C}^4).$$

Note that we are using atomic units in this paper, i.e., $m_e = \hbar = e = 1$.

As an immediate consequence of the work of Evans et al. [2] this form is bounded from below, in fact it is positive (Tix [21, 22]), if $\kappa := Z/c \leq \kappa_{\text{crit}} := 2/(\pi/2 + 2/\pi)$. (In the following, we will assume that the ratio $\kappa \in [0, \kappa_{\text{crit}})$ is fixed.) According to Friedrichs this allows us to define a self-adjoint operator $B_{c,N,Z}$ whose ground state energy

$$(4) \qquad E(c, N, Z) := \inf \sigma(B_{c,N,Z}) = \inf\{\mathcal{E}(\psi) | \psi \in \mathfrak{Q}_N, \|\psi\| = 1\}$$

is of concern to us in this paper. In fact – denoting by $E_{\text{TF}}(Z, Z)$ the Thomas-Fermi energy of Z electrons in the field of nucleus with atomic number Z and $q = 2$ spin states per electron – our main result is

Theorem 2. *For given* $\kappa = Z/c \in [0, 2/\pi]$ *and* Z *tending to infinity*

$$E(Z/\kappa, Z, Z) = E_{\text{TF}}(Z, Z) + o(Z^{7/3}).$$

This result, given here for the neutral atomic case, has obvious generalizations to ions and molecules. To keep the presentation short we refrain from presenting them here, as their treatment follows the same strategy.

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The Relativistic Scott Correction

Jan Philip Solovej

(joint work with T. Østergaard Sørensen and W. L. Spitzer)

In this talk we discuss the relativistic Scott correction. For simplicity we restrict the discussion to atoms although similar results can be proved for molecules (see [11]).

The starting point is the Hamiltonian for an atom with nuclear charge Z s

$$H_{N,Z} = \sum_{i=1}^{N} \left(T_i - \frac{Z}{|x_i|} \right) + \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|}.$$

Here N is the number of electrons and $x_i \in \mathbb{R}^3$, $i = 1, \ldots, N$ are the electron coordinates. We shall specify the kinetic energy operators T_i acting on functions of x_i below. We are actually interested in the neutral case, when the number of electrons N is equal to Z. For simplicity and to avoid complications if Z is not an integer, in which case exact neutrality cannot be achieved, we shall here consider

the *ground state energy* defined by

$$E(Z) = \inf\{(\Psi, H_{N,Z}\Psi) \quad | \quad \Psi \text{ anti-symmetric } N\text{-body wave function,}$$

$$\int |\Psi|^2 = 1, N = 1, 2 \ldots\}.$$

Thus $E(Z)$ is the energy minimized over particle number N. Our main result below holds also for the neutral case. The wave functions Ψ above are functions of the electron coordinates $x_i \in \mathbb{R}^3$ and the electron spin $\sigma_i = \pm 1$. They are anti-symmetric when two particle indices i, j are interchanged. The energy infimum will not be affected if we restrict to wave functions that are smooth.

In the non-relativistic case we take the kinetic energy operators to be $T_i = -\frac{1}{2}\Delta_i$. We are using units in which Planck's constant $\hbar$ and the mass and charge of the electron are all chosen to be 1. In this case the ground state energy, which we denote $E_{\mathrm{nr}}(Z)$, has an asymptotic expansion for large Z given by

$$E_{\mathrm{nr}}(Z) = -C_{\mathrm{TF}}Z^{7/3} + \frac{1}{2}Z^2 + C_{\mathrm{DS}}Z^{5/3} + o(Z^{5/3})$$

as $Z \to \infty$. The leading term was predicted by Thomas [13] and Fermi [3] and proved rigorously by Lieb and Simon [6]. The second term is the Scott term predicted by Scott [7] and proved rigorously by Hughes [4] (lower bound) and Siedentop and Weikard [8]. The third term was predicted by Schwinger [10] relying on a result of Dirac [1]. It was proved rigorously by Fefferman and Seco [2]. The non-relativistic Scott correction for molecules was proved by Ivrii and Sigal [5].

The main result of this talk is to generalize the Scott term to a relativistic situation. Unfortunately, we do not have a mathematically satisfactory formulation of relativistic quantum mechanics. We will instead consider a simplified model, which we hope has some correct qualitative characteristics of a relativistic quantum theory. Our model is arrived at by replacing the non-relativisic kinetic energy operators given above by the corresponding operators deduced from Einsteins formula $T_i = \sqrt{-c^2\Delta_i + c^4} - c^2$. Recall that we are using units in which the mass of the electron and Planck's constant are 1. In these units the physical value of c, the speed of light, is approximately 137. We shall however think of c as a large parameter which we will let tend to infinity.

It is a fact that if $Z/c > \frac{2}{\pi}$, then the operator $H_{N,Z}$ above is not bounded below (if originally defined on smooth compactly supported functions), i.e., the ground state energy defined above is $-\infty$. If $Z/c \leq \frac{2}{\pi}$ then the ground state energy, which we now denote $E_{\mathrm{r}}(Z)$ (suppressing its dependence on c) is finite.

Thus we cannot consider the limit of $E_{\mathrm{r}}(Z)$ as $Z \to \infty$ for fixed c. Instead we will consider the limit $Z \to \infty$, $c \to \infty$ with Z/c fixed. A similar limit was studied by Schwinger [9]. Our main result in [11] is stated in the next theorem.

Theorem 4. *There exists a function* $S : [0, 2/\pi) \to \mathbb{R}$ *such that*

$$E_{\mathrm{r}}(Z) = -C_{\mathrm{TF}}Z^{7/3} + \frac{1}{2}Z^2 S(Z/c) + o(Z^2)$$

as $Z \to \infty$, $c \to \infty$ with $Z/c \leq \nu < 2/\pi$. The error term $o(Z^2)$ depends only on the parameter ν.

The constant C_{TF} in this theorem is the same as in the non-relativistic case as realized by Sørensen in [12]

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Quantum Chemistry using Numerical Orbitals

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Progress on an ongoing research program to develop and improve methods for using numerical defined basis orbitals in molecular structure calculations will be reported. In the usually MO-LCAO approach single-particle electron wave functions are expanded in the form

$$(1) \qquad \phi_i(\mathbf{r}) = \sum_j c_{ji} \chi_j(\mathbf{r} - \mathbf{R}_j).$$

The $\chi_j(\mathbf{r} - \mathbf{R}_j)$ are superpositions of Gauss-type orbitals (GTOs) and the $\mathbf{R}_j$ are usually the nuclear coordinates. The GTOs are used since they make the determination of the various matrix elements required almost trivial. On the other hand, they are not particularly suitable for the description of various electronic properties, such as the electron density at the nuclei, and at large distances.

In this project, the basis orbitals χ_j are instead taken to be numerically defined on a mesh centered on the associated nucleus. This permits the variational optimization of the orbitals, thereby drastically reducing the size of the required basis set. The corresponding optimization with GTOs is rarely attempted. The basic problem then is to obtain the multicenter integrals required in electron structure calculations:

$$(2) \qquad \omega_{ij} = \int \chi_i(\mathbf{r} - \mathbf{R}_i)\chi_j(\mathbf{r} - \mathbf{R}_j)d\mathbf{r}$$

$$(3) \qquad V_{Nkm} = \int \chi_k(\mathbf{r} - \mathbf{R}_k)\frac{1}{|\mathbf{r} - \mathbf{R}_N|}\chi_m(\mathbf{r} - \mathbf{R}_m)d\mathbf{r}$$

$$(4) \quad v(kl, mn) = \int \chi_k(\mathbf{r} - \mathbf{R}_k)\chi_l(\mathbf{r}' - \mathbf{R}_l)\frac{1}{|\mathbf{r} - \mathbf{r}'|}\chi_m(\mathbf{r} - \mathbf{R}_m)\chi_n(\mathbf{r}' - \mathbf{R}_n)d\mathbf{r}d\mathbf{r}'$$

the overlap, nuclear attraction and electron-electron repulsion integrals.

The essential strategy is to employ a translation formula that can be written, if $f_{lm}(\mathbf{r}) = f(r)Y_{lm}(\hat{\mathbf{r}})$,

$$f_{lm}(\mathbf{r} - \mathbf{R}) = \sum_{LL'MM'} (2L + 1)(2L' + 1)R(lLL'mMM')$$
$$(5) \qquad\qquad\qquad \times Y_{LM}(\mathbf{r})Y_{L'M'}(\mathbf{R})F_{LL'}(r, R; f)$$

where

$$(6) \qquad F_{LL'}(r, R; f) = \frac{2}{\pi}i^{l+L'-L}\int_0^\infty j_L(kr)j_{L'}(kR)\tilde{f}(k)k^2 dk$$

and

$$(7) \qquad \tilde{f}(k) = \int_0^\infty j_l(kr)f_l(r)r^2 dr.$$

The coefficients $R(lLL'mMM')$ are expressible in terms of $3 - j$ or Gaunt coefficients. The sum is necessarily truncated at some $L = L_{max}$.

A method [1] has been developed that permits the very efficient and accurate calculation of the functions $F_{LL'}(r, R; f_l)$. This permits the calculation of the overlap integrals of Eq. (2) in a simple way.

The nuclear attraction integrals are obtained by expanding each factor about a center that is chosen to optimize the convergence rate of the resulting series [2]. In the case of CH_4, $L_{max} = 6$ yields mH accuracy.

The electron-electron repulsion integrals are obtained by interpreting them as the electrostatic energy of two charge distributions defined by the orbital products [3]. Each charge distribution is obtained by expanding the orbital factors about the mid-point between their centers, and multiplying the two expansions. The product can be reduced by using the standard identity for the expansion of a product of spherical harmonics. The resultant integral for the matrix element is evaluated in momentum space.

These methods for obtaining the necessary integrals for arbitrary orbitals lead to the possibility of variationally optimizing the orbitals. The Euler- Lagrange

equations for the orbitals subject to the constraint that the molecular orbitals ϕ_i remain orthonormal can be derived and lead to a system of coupled inhomogeneous equations that resemble the Schroedinger equation [4]. The Hartree-Fock self-consistency problem, and the orbital optimizations are solved iteratively.

The program also includes the determination of the energy gradients with respect to the nuclear coordinates. However, the Hessian matrix problem has proved to be intractable.

Preliminary work has also been carried out on applying the approach in DFT LDA calculations for molecules [5].

The advantages of the approach are that the wave functions give a much better description of the electron behavior at the nuclei and at large distance, and that much smaller basis sets are required in comparison with the GTO method at a given level of accuracy. In addition, since the wave functions can approximate HF wave functions much more accurately, the so-called basis set superposition error, should be much smaller or negligible.

As an example, the HF problem for CH_4 has been solved in the minimal basis of $1s, 2s, 2p$ orbitals on C and $1s$ orbitals on H. Eight orbital optimizations and total energy calculations required 65 second on an HP laptop. The resulting energy is ≈ 28 mH above the estimate obtained in the pV6Z basis set [6].

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A rigorous surface hopping algorithm for propagation through conical crossings

STEFAN TEUFEL

(joint work with C. Lasser and T. Swart)

We consider the standard model problem for propagation through a conical intersection of electronic surfaces in molecular dynamics, namely the time-dependent Schrödinger equation $i\varepsilon\frac{d}{dt}\psi^\varepsilon(t) = H^\varepsilon\psi^\varepsilon(t)$, $\psi^\varepsilon(0) \in L^2(\mathbb{R}^2, \mathbb{C}^2)$, with Hamiltonian operator $H^\varepsilon = -\frac{\varepsilon^2}{2}\Delta \otimes \mathbf{1}_{\mathbb{C}^2} + \begin{pmatrix} x_1 & x_2 \\ x_2 & -x_1 \end{pmatrix}$. The eigenvalues $\pm|x|$ of the potential matrix display a conical crossing at $x = 0$. Our main result is the construction of a semigroup that approximates the Wigner function associated with the solution of the Schrödinger equation at leading order in the semiclassical parameter ε. The semigroup stems from an underlying Markov process which combines deterministic transport along classical trajectories within the electronic

surfaces and random jumps between the surfaces near the crossing. Our semi-group can be viewed as a rigorous mathematical counterpart of so-called tra-jectory surface hopping algorithms, which are of major importance in chemical physics' molecular simulations. The key point of our analysis, the incorporation of the non-adiabatic transitions, is based on the Landau-Zener type formula of Fermanian-Kammerer and Gérard [1] for the propagation of two-scale Wigner measures through conical crossings.

We also compare numerical solutions of the Schrödinger equation to numerical solutions of the surface hopping algorithm, both numerically converged, in order to test the validity of the semigroup in realistic settings. For a wide range of parameters the systematic error of our surface hopping algorithm is below 2%.

The mathematical results are published in [2], the numerical results are available as a preprint [3].

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Optimised effective potentials in magnetic response calculations

David J. Tozer

(joint work with A. M. Teale, A. J. Cohen, O. B. Lutnaes, T. Helgaker)

There is currently much interest in the determination of uncoupled, second-order magnetic response properties in density functional theory, using hybrid exchange-correlation functionals with multiplicative exchange-correlation potentials [1, 2, 3, 4, 5]. For main-group nuclei, high quality results have been obtained using potentials from the constrained search and optimised effective potential (OEP) approaches [6, 7].

In this work, we investigate whether similar improvements are obtained for transition metal chemical shifts, which are a significant challenge for theoretical methods. Specifically, we use the Yang-Yu [8] implementation of the OEP, in which the Kohn-Sham potential is written $v_s(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_0(\mathbf{r}) + \sum_t b_t g_t(\mathbf{r})$, where $v_{ext}(\mathbf{r})$ is the external potential, $v_0(\mathbf{r})$ is a fixed reference potential, and the final term is an expansion in a Gaussian basis set. Our calculations highlight the importance of a well-chosen reference potential and the sensitivity of the results to the choice of potential expansion. In particular, special care is required to avoid unphysical structure in the exchange-correlation potentials when hybrid function-als are used and this is consistent with a number of other recent studies [9, 10]. We avoid this structure in the present work through a judicious choice of cutoff in the

singular value decomposition. Our results demonstrate that the use of the OEP approach does lead to notable improvements in chemical shifts. For full details, see Ref. [11].

In addition to chemical shifts, we demonstrate that the uncoupled OEP approach also leads to very high quality rotational g tensors, which quantify the shift in rotational energy levels when a molecule is placed in an external magnetic field. The results surpass those from a functional that was specifically designed to yield high quality magnetic response parameters. For full details, see Ref. [12].

Finally, we highlight unexpected differences between the rigorous OEP exchange potentials and approximate potentials determined using the localised Hartree-Fock (LHF) [13] approach. By comparing with near-exact quantities, we demonstrate that the differences mimic the effect of electron correlation, which is consistent with the observation that LHF shielding constants are in rather good agreement with experimental values, despite the absence of an explicit correlation functional. For full details, see Ref. [14].

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Regularity properties and the hyperbolic cross space approximation 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 atomar 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.

The problem with this equation is its high dimensionality which immediately rules out standard discretization methods like finite differences or finite elements. Current approximation methods, with the Hartree-Fock methods and the density functional theory based methods as the classical examples, are used with much success, but more resemble simplified models than true discretization methods in the sense of numerical analysis. The regularity theorems in [Y1], [Y3] might form a possible point of attack for the construction of such direct methods. To some degree, they also underpin the orbital picture of atoms and molecules and explain why Hartree-Fock-methods work so well.

To state these regularity theorems, one has to keep two things in mind. First, that the bottom of the essential spectrum of the electronic Schrödinger operator is less than or equal to zero. Therefore the eigenfunctions for negative eigenvalues are of main interest in quantum chemistry. We restrict ourselves to such eigenfunctions. Secondly, the true wavefunctions do not only depend on the positions but also on the spins of the electrons and are, by the Pauli principle, antisymmetric with respect to the simultaneous exchange of the electron positions and spins. The admissible solutions of the electronic Schrödinger equation are those that are components of such a full spin-dependent wavefunction. This means that every such solution is antisymmetric with respect to the exchange of the positions of the electrons of same spin and vanishes where two such electrons meet. In the sequel, the sets I_- and I_+ of the indices associated with the electrons with spin up and spin down are fixed. For $s=0$ and $s=1$, let

$$
\|u\|_{\pm,s}^2 = \int \Big(\sum_{i=1}^{N}|\frac{\omega_i}{\Omega}|^2\Big)^s \prod_{i\in I_\pm}\Big(1+|\frac{\omega_i}{\Omega}|^2\Big)\,|\widehat{u}(\omega)|^2\,d\omega,
$$

with $\omega_i \in \mathbb{R}^3$ the momentum of the electron i and Ω a scaling parameter. The norms given by this expression are composed the L_2-norms of certain high-order mixed derivatives, the maximum order of which increases with the number of electrons. In [Y1] it has been proved that the given eigenfunctions are located in the corresponding Hilbert spaces and are therefore much smoother as one might first expect. In [Y3] we could recently quantify this result and estimate the norms of these mixed derivatives in terms of the L_2-norm of the eigenfunctions. For

$$\Omega \geq 4C\sqrt{N} \max(N, Z),$$

the given eigenfunctions satisfy the estimates

$$\|u\|_{\pm,0} \leq \sqrt{2e}\, \|u\|_0, \quad \|u\|_{\pm,1} \leq \sqrt{2e}\, \|u\|_0,$$

where C is a small generic constant that neither depends on the number N of the electrons nor on the total charge Z of the nuclei or their positions.

The minimum $\Omega \leq 4C\sqrt{N} \max(N, Z)$ for which these estimates hold for all eigenfunctions of the described kind fixes an intrinsic length scale of the considered atomar or molecular system. Length scales like this naturally appear in estimates that relate derivatives of distinct order to each other. Such length scales have to be incorporated in the definition of the corresponding norms to compensate the different scaling behavior of the derivatives and to obtain estimates that are independent of the choice of units. The crucial point here is that the given upper bound for the optimal scaling parameter is both independent of the particular eigenfunction and of the number, the charge, and the position of the nuclei. The proof of this theorem is based on a mixture of variational arguments and Fourier analysis and essentially utilizes the fact that the wavefunctions vanish where electrons with same spin meet. The analysis of simplified models in which the electron-electron interaction is neglected shows that our upper estimate for the minimum Ω can in general probably not be improved, but also suggests that this estimate is far too pessimistic for bigger molecules consisting of many atoms.

The estimates above mean that the Fourier transforms of the eigenfunctions are concentrated around the cartesian products of the hyperbolic crosses

$$\prod_{i \in I_-} \left(1 + |\frac{\omega_i}{\Omega}|^2\right) \leq R^2, \quad \prod_{i \in I_+} \left(1 + |\frac{\omega_i}{\Omega}|^2\right) \leq R^2,$$

that is, along 3- respectively 6-dimensional coordinate spaces. The wavefunctions behave in this respect similarly as products of three-dimensional orbitals, that is, as Hartree-Fock methods anticipate and chemists always believed. To quantify this, let χ_R be the characteristic function of the domain above and

$$(P_R u)(x) = \left(\frac{1}{\sqrt{2\pi}}\right)^{3N} \int \chi_R(\omega)\widehat{u}(\omega) \exp(\mathrm{i}\,\omega \cdot x)\, d\omega$$

the projection of a function u onto the space of functions with Fourier transforms vanishing outside this region. For all eigenfunctions u of the given kind then

$$\|u - P_R u\|_0 \leq \frac{2\sqrt{e}}{R}\, \|u\|_0, \quad |\,u - P_R u\,|_1 \leq \frac{2\sqrt{e}}{R}\, \Omega\, \|u\|_0.$$

For R chosen sufficiently large, it suffices therefore to look for approximation spaces that are able to approximate the projections $P_R u$ or similar parts of the eigenfunctions u well and to neglect the other frequency components. This is a much simpler task than to approximate functions in the full space.

Sparse grid type functions are very well suited to this purpose. A construction of this kind has been presented in [Y3], where the scaling discussed here has still to be built in. The idea is to replace the function χ_R above by a superposition

$$\chi_R(\omega) \leq \sum_l \chi^{(l)}(\omega) \leq 1$$

of functions $\chi^{(l)}$ of tensor product structure. The factors of which the $\chi^{(l)}$ are composed cut off single frequency bands. The function with the Fourier transform

$$\omega \to \sum_l \chi^{(l)}(\omega)\,\widehat{u}(\omega)$$

then approximates u at least as well as the projection $P_R u$. The single parts on the right hand side are then approximated separately, making use of the fact that the Fourier transforms of the eigenfunctions are infinitely differentiable. To keep the number of degrees of freedom under control, the symmetry properties of the wavefunctions inevitably have to be taken into account [Y4].

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Optimized Effective Potentials

Weitao Yang

(joint work with T. Heaton-Burgess, F. A. Bulat)

Kohn-Sham density functional theory (KS DFT) [1] enjoys wide application owing to the computational accessibility afforded by formulating the many body problem in terms of the noninteracting KS reference system. However, the exact exchange-correlation energy functional E_{xc} and corresponding local potential, v_{xc}, are unknown. The future success of DFT is dependent on the availability of suitable approximations for E_{xc}. Significant interest is being shown for the development of implicit density functionals, depending explicitly on the KS orbitals [2]. For such functionals, v_{xc} cannot be directly obtained as a simple functional derivative and requires an OEP method for its determination [3, 4, 5].

The OEP concept first appeared within the Hartree-Fock (HF) formalism [6], and later was employed in DFT [7] using the HF exact exchange energy functional (EXX). These conventional approaches identify the local KS potential for exact

exchange as that obtained from solving $\delta E[\{\phi_i^{\mathrm{KS}}\}]/\delta v_s(\mathbf{r}) = 0$, which in turn leads to a linear integral equation to be solved for the OEP. The rigorous justification of the OEP method as a variational minimization has however only recently been provided within the potential functional formulation [8]. This formulation lends itself to a direct approach to solving for the OEP [5] where the minimization of the energy functional over local potentials is considered.

The discrete representation of the OEP problem in finite basis sets for both the Kohn-Sham orbitals and the potential can be ill-posed [9, 10]: While the total OEP energy is stable with respect to the changes in the potential, there can be many different potentials, including nonphysical ones, having numerically degenerate total energies. This has lead to some degree of confusion of what in fact constitutes a valid, finite basis, OEP implementation [10]. Up to now, the origin of this ill-posedness has been unaccounted for.

We will show that the ill-posed nature of the discrete OEP originates from the use of unbalanced basis sets. This ill-posedness does not imply that the OEP method is unphysical by construction, rather, just that it can lead to nonphysical potentials. The regularization method developed in this work insures that the physical context of finite basis OEP calculations are maintained in all cases, with generation of physically meaningful potentials.

Our OEP implementation is the direct optimization approach of Yang and Wu [5] where the trial potential is expanded in a finite basis set, $\{g_t\}$, as $v_s^\sigma(\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + v_0(\mathbf{r}) + \sum_t b_t^\sigma g_t(\mathbf{r})$. Here v_{ext} is the external potential of the system under consideration and v_0 is a fixed reference potential, taken as the Fermi-Amaldi potential (or the Coulomb potential for LDA) for the sum of the atomic densities so to enforce the correct asymptotic behavior upon v_s. Transferring the functional dependence from the KS potential on to the expansion coefficients $\{b_t^\sigma\}$ in this way gives rise to an efficient implementation of the OEP based on the unconstrained minimization of $E(\{b_t^\sigma\})$ with readily available analytic derivatives [5].

We take the classical approach to ill-posed problems and further incorporate some desirable measure to regularize the solution [11]. It is clear that any nonphysical oscillatory behavior in the potential will be confined to the basis set expansion $v_\mathbf{b} = \sum_t b_t g_t$. We thus introduce a λ–regularization by constraining our solutions to yield smooth potentials as measured by the *smoothing norm* $||\nabla v_\mathbf{b}||$, thereby restricting the nonphysical variations in the potential because of unbalanced basis set. This norm is certainly not unique, however is simple to implement and will be seen to produce very satisfying results. We define a regularized energy functional as

(1) $$\Omega_\lambda(\mathbf{b}) = E^{\mathrm{YW}}(\mathbf{b}) + \lambda||\nabla v_\mathbf{b}(\mathbf{r})||^2,$$

where $||\nabla v_\mathbf{b}(\mathbf{r})||^2 = 2\mathbf{b}^{\mathrm{T}}\mathbf{T}\mathbf{b}$, $\mathbf{T}$ is the kinetic energy integral matrix in the potential basis and $E^{\mathrm{YW}}(\mathbf{b})$ is the OEP energy calculated according to the Yang-Wu procedure. The energy derivatives with respect to the coefficients are modified accordingly as $\nabla_\mathbf{b}\Omega_\lambda = \nabla_\mathbf{b}E^{\mathrm{YW}} + 4\lambda\mathbf{T}\mathbf{b}$ and $\nabla_\mathbf{b}^2\Omega_\lambda = \nabla_\mathbf{b}^2 E^{\mathrm{YW}} + 4\lambda\mathbf{T}$.

This regularization procedure, together with an L-curve analysis, allows us to determine the physically meaningful OEP potential and energy from calculations performed with any basis sets, as shown for numerous examples of atoms and molecules. Our work also calls for the construction of balanced potential basis sets for efficient OEP calculations.

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Order N methods in electronic structure calculations at finite temperature

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(joint work with S. Le Roux)

. The recursion method is an orbital free method, and is therefore adapted to systems for which such calculations would lead to very large computation times. This is for example the case of high temperature plasmas, where the broadening of the Fermi-Dirac distribution leads to a rapid increase of the number of populated states. This size has so far limited the temperature range which has been covered by *Ab initio* molecular dynamics methods where the electrons receive full quantum mechanical treatment and the ions are propagated classically on the resulting

energy surface. While this approach has been extensively used in the past ten years in this field and was rather successful at computing the physical properties of dense plasmas, [4, 5, 6, 7] it has only been possible to perform simulations above 10 eV or so by resorting to approximate expressions of the kinetic energy functional.[8]

An alternative setting of the recursion method, more easily extensible toward high temperatures, has been devised by Baroni and Giannozzi[9], in which the electronic density is directly computed on a regular mesh in real space. This method is therefore well suited for an implementation in the Kohn-Sham formalism, since the electronic density is the central quantity in this formalism, and the basis set can be easily increased to achieve convergence. A variant of this approach was later elaborated, which relies on a direct evaluation of the diagonal elements of the Fermi density matrix operator at finite temperature. Fermi density matrix [15]:

$$(1) \qquad \rho(\mathbf{r}) = <\mathbf{r}|\frac{1}{1 + e^{\beta(H-\mu)}}|\mathbf{r}>$$

This electronic density is approximated as:

$$
\begin{aligned}
\rho_h(\mathbf{r}_i) &= \frac{1}{h^3} < u_0^{i,h}|\frac{1}{1 + e^{\beta(H-\mu)}}|u_0^{i,h} > \\
&= \frac{1}{h^3}\left(< u_0^{i,h}|1|u_0^{i,h} > - < u_0^{i,h}|\frac{1}{1 + e^{-\beta(H-\mu)}}|u_0^{i,h} > \right)
\end{aligned}
$$

where $u_0^{i,h}$ is an approximation of the Dirac delta function. The last term of this expression is put in tridiagonal form according to the Lanczos procedure:

$$e^{-\beta(H-\mu)}u_n^{i,h} = b_n^{i,h}u_{n-1}^{i,h} + a_n^{i,h}u_n^{i,h} + b_{n+1}^{i,h}u_{n+1}^{i,h}$$

and can be computed as a continued fraction as:

$$(2) \qquad h^3\rho_h(\mathbf{r}_i) = 1 + \cfrac{1}{-1 - a_0 - \cfrac{b_1^2}{-1 - a_1 - \cfrac{b_2^2}{\ddots}}}$$

noted $1 + \sum_{k=0}^{\infty}(-b_k^2)|(-1 - a_k)$.

This approach has already been presented in a previous paper [12], but no assessment of its numerical properties were given at the time.

The aim of the present work is to analyze the convergence properties of this latter method in many respects:

- Understand the convergence properties
- Establish an error estimate
- Analyze the "locality properties"

This assessment has been made using two examples: the free electron gas and the helium plasma.

In the course of this research, we have established someproperties of the method. First,it is possible to obtain quite high an accuracy, at least in the studied cases. We think this is due to the use of the exponential of the Hamiltonian, a compact operator, for which convergence properties of the recursion coefficients is guaranteed. Second, the method is stable, Third, an accurate and easy to compute estimate of the error has been devised, a particularly useful property when performing practical calculations.

Finally, the growth of the recursion vector, can be evaluated and,this allows to effectively truncate the recursion vector and perform calculation with order N scaling.

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