Mathematical models and some challenges in quantum chemistry

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Tutorial

Workshop 'Density Functional Theory: Fundamentals and Applications in Condensed Matter Physics', Organizers: E. Cancès, C.J.Garcia-Cervera, Y.A.Wang

Banff, 24.1.2011

2. Approximations and reduced models

Starting point

Exact (non-relativistic, Born-Oppenheimer) N-electron eq. known

$$H\psi = E\psi, \quad \psi = \psi(x_1, .., x_N; s_1, .., s_N), \quad \psi \text{ antisymm.}$$

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Recall electronic Hamiltonian:

$$H = T_e + V_{ne} + V_{ee}$$

with

$$T_e = \sum_i (-\frac{1}{2}\Delta_{x_i}), \; V_{ne} = \sum_i v_{ne}(x_i), \; V_{ee} = \sum_{i<j} |x_i - x_j|^{-1}$$

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Many reduced models exploit the variational formula for the lowest eigenvalue of H:

$$E = \min_{\psi \in \mathcal{A}} \langle \psi | H | \psi \rangle$$

where ψ is varied over the admissible set

$$\mathcal{A} = \{ \psi \in H^1((\mathbb{R}^3 \times \mathbb{Z}_2)^N) \, | \, \psi \text{ antisymmetric}, \; \langle \psi | \psi \rangle = 1 \}.$$

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$$\mathcal{S} = \{ |\psi_1 \cdots \psi_N\rangle \,|\, \psi_1, .., \psi_N \in H^1(\mathbb{R}^3 \times \mathbb{Z}_2), \, \langle \psi_i | \psi_j \rangle = \delta_{ij} \}$$

(set of Slater determinants), with

$$|\psi_1 \cdots \psi_N\rangle(x_1, .., x_N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \psi_1(x_1) & \cdots & \psi_1(x_N) \\ \vdots & & \vdots \\ \psi_N(x_1) & \cdots & \psi_N(x_N) \end{pmatrix}$$

Hartree-Fock model, ctd.

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Energy functional as a function of the orbitals: Notation: $x = (r, s) \in \mathbb{R}^3 \times \mathbb{Z}_2$

$$\begin{aligned}\langle\psi|H|\psi\rangle &= \sum_i \langle\psi_i| -\tfrac{1}{2}\Delta + v_{ne}|\psi_i\rangle \\ &+ \frac{1}{2}\sum_{i,j}\int\int \frac{|\psi_i(x)|^2|\psi_j(x')|^2 - \psi_i(x)\overline{\psi_j(x)}\psi_j(x')\overline{\psi_i(x')}}{|r-r'|}\,dx\,dx'\end{aligned}$$

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Euler-Lagrange equations (Hartree-Fock equations):

$$f_\psi \psi_i = \epsilon_i \psi_i \quad (i = 1, .., N)$$

with the Fock operator

$$f_\psi \phi = \Big(-\frac{1}{2}\Delta + v_{ne} + \int \sum_i \frac{|\psi_i(x')|^2}{|\cdot - r'|}dx'\Big)\phi - \int \sum_i \frac{\phi(x')\overline{\psi_i(x')}}{|\cdot - r'|}dx'\Big)\psi_i$$

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Easy to show that $\epsilon_1, .., \epsilon_N$ are the lowest eigenvalues of f_ψ. This follows from positivity of the Hessian at a minimizer.

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This is because HF energy and Fock operator depend only on the projector (density matrix)

$$\sum_{i=1}^{N} |\psi_i\rangle \langle\psi_i| =: \gamma_\psi.$$

In particular, identifying γ_ψ with its integral kernel $\gamma_\psi(x,x')$ (and recalling $x' = (r',s')$)

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Roothaan algorithm (Roothaan 1955, math. analysis: Cancès/LeBris 2000)

$$\gamma_{k+1} = \chi_{(-\infty,\epsilon_{max}]}(f_{\gamma_k}).$$

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Remark from audience (G.Scuseria):
For molecules, even total energies can be poor, as in H_2.

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$\Psi_o =$ HF ground state $= |\psi_1 \cdots \psi_N\rangle$ (fixed)
$\psi_{N+1}, ..., \psi_K$ next (unoccupied) eigenstates of f_{Ψ_0} (fixed)
$\Psi_i^a = |\psi_1 \cdots \psi_{i-1}\, \psi_a\, \psi_{i+1} \cdots \psi_N\rangle$ ($i \le N$, $a \ge N+1$) excitation

$$\mathcal{A}^{CI} \;=\; \Big\{ \Psi = c\Psi_0 + \sum_{i,a} c_{ia}\Psi_i^a + \tfrac{1}{4} \sum_{i,j,a,b} c_{ij}^{ab}\Psi_{ij}^{ab} + ... \Big| \; c,\, c_i^a,\, c_{ij}^{ab}, ... \in \mathbb{C},\, \langle\Psi|\Psi\rangle = 1 \Big\}$$

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Thus, in CI we minimize over only expansion coefficients, while in MCSCF we minimize over orbitals and expansion coefficients.

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$T = T_1 + T_2 + \ldots$ cluster operator

$T_1 \Psi_0 = \sum_{i,a} t_i^a \Psi_i^a$ Second quantized notation: $T_1 = \sum_{i,a} t_i^a \mathbf{a}^\dagger(a)\, \mathbf{a}(i)$

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where the coefficients t_i^a, t_{ij}^{ab}, ... in T solve the amplitude equations

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Eqns nonlinear, no variational structure

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DFT−LDA

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Basic version of DFT.

Mathematically: similar to HF model, except the nonlocal exchange term is replaced by a local exchange-correlation term.

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with admissible set

$$\mathcal{A}^{DFT} = \{(\phi_1, .., \phi_N) \in H^1(\mathbb{R}^3 \times \mathbb{Z}_2))^N \,|\, \langle \phi_i | \phi_j \rangle = \delta_{ij}\}$$

(Kohn-Sham orbitals) and energy functional

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where $\rho(r) = \sum_s \sum_i |\phi_i(r,s)|^2$ (density) and ε_{xc} is a “known” function of ρ (exchange-correlation energy density of a homog.el.gas with density ρ).

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Euler-Lagrange equations: (system of N coupled nonlinear PDE's in $\mathbb{R}^3$)

$$f_\rho \phi_i = \epsilon_i \phi_i \quad i = 1, .., N$$

with the Kohn-Sham operator

$$f_\rho = -\frac{1}{2}\Delta + v_{ne} + \int \frac{1}{|\cdot - r'|} \rho(r')\, dr' + \frac{d\varepsilon_{xc}(\rho)}{d\rho}.$$

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FCI	$\binom{K}{N}$	$\sim N^{-1/2} const^N$

3. Mathematical challenges

other than designing the perfect E_{xc} which everybody would want to use

Challenge 1: Representability

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In particular, re-derive known bounds (such as Erdahl's 3-index-conditions) by a systematic method, rather than *Guess-And-Verify*.

In fact, even the nec. and suff. bounds on one-body DM's are only derived by Guess-And-Verify.

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- occupied core orbitals
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That's why wavefunction methods designed by chemists beat, e.g., clever general-purpuse sparse grid methods by mathematicians, hands down.

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(But beware of the difficulties with established explicitly correlated methods and emerging sparse methods.)

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Remark from audience (K.Burke):
'Pure luck' is perhaps an overstatement. When first introducing DFT, Walter Kohn – with his background in solid-state physics – did have applicability to solids in mind.

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Example (experimental data)

Atom	Li	Be	B	C	N	O	F	Ne	Cr
Ratio of first spectral gap to ground state energy	0.0093	0.0068	0.0053	0.0012	0.0016	0.00096	0.0078	0.0047	0.00003

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- Identify and analyze suitable asymptotic limit in which $\frac{gap}{total\ en.} \to 0$ (here: $Z \to \infty$ at fixed N)

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- Use the method to correcty predict interconfigurational ordering of transition metal atoms (missed by standard methods)

  Ch.Mendl, GF, J.Chem.Phys. 133, 184101, 2010

Orbital filling, 3d transition metal series, various methods

Atom	Madelung	HF	Rel.HF	LSDA	Becke 88	B3LYP	Expt.
Sc	$4s^2 3d^1$	$4s^2 3d^1$	$4s^2 3d^1$	$4s^2 3d^1$	$4s^2 3d^1$	$4s^2 3d^1$	$4s^2 3d^1$
Ti	$4s^2 3d^2$	$4s^2 3d^2$	$4s^2 3d^2$	$4s^2 3d^2$	$4s^1 3d^3$	$4s^2 3d^2$	$4s^2 3d^2$
V	$4s^2 3d^3$	$4s^2 3d^3$	$4s^2 3d^3$	$4s^1 3d^4$	$4s^1 3d^4$	$4s^1 3d^4$	$4s^2 3d^3$
Cr	$4s^2 3d^4$	$4s^2 3d^4$	$4s^1 3d^5$	$4s^1 3d^5$	$4s^1 3d^5$	$4s^1 3d^5$	$4s^1 3d^5$
Mn	$4s^2 3d^5$	$4s^2 3d^5$	$4s^1 3d^6$	$4s^2 3d^5$	$4s^2 3d^5$	$4s^2 3d^5$	$4s^2 3d^5$
Fe	$4s^2 3d^6$	$4s^2 3d^6$	$4s^1 3d^7$	$4s^2 3d^6$	$4s^2 3d^6$	$4s^2 3d^6$	$4s^2 3d^6$
Co	$4s^2 3d^7$	$4s^2 3d^7$	$4s^2 3d^7$	$4s^1 3d^8$	$4s^2 3d^7$	$4s^1 3d^8$	$4s^2 3d^7$
Ni	$4s^2 3d^8$	$4s^2 3d^8$	$4s^1 3d^9$	$4s^1 3d^9$	$4s^1 3d^9$	$4s^1 3d^9$	$4s^2 3d^8$
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Blue: The first two of the 20 experimental ‘anomalies’ w.r.to the Madelung rule (fill via $n+\ell \sim$no. of WF nodes)

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Ch.Mendl, GF, J.Chem.Phys. 133, 184101, 2010: anomalous filling order correctly predicted via asymptotics-based CI method

Open: correct prediction via an asymptotics-based DFT

Challenge 5, ctd: List of interesting asymptotic limits

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Isoelectronic limit atomic ions, N fixed, Z$\rightarrow \infty$

Hylleraas, Layzer, Wilson, G.F., Goddard, Mendl

Quantum oscillations, shell structure, electron correlation

Thomas-Fermi limit neutral atoms, N=Z$\rightarrow \infty$

Lieb, Simon, Scott, Siedentop/Weikard, Hughes, Bach, Fefferman/Seco, Burke

Basic prototype of DFT, averaged semiclassics

Dissociation limit $|R_A - R_B| \rightarrow \infty$

London, Casimir/Polder, ...

Leading order van der Waals term not captured by any standard DFT

Coalescence limit $r_{12} \rightarrow 0$

Kato, Soerensen et al, N.R.Hill, Kutzelnigg, Goddard

Slow convergence of CI and related expansions

Thermodynamic limit $N \rightarrow \infty$, $vol \rightarrow \infty$, $\frac{N}{vol} = const$

Lieb/Lebowitz, Fefferman, Ceperley/Alder, Catto/Le Bris/Lions, Hainzl/Lewin/Solovej, Cancès/Deleurence/Lewin, ...

'stability of matter', 'size consistency', energy of defects

My current other favourite $\hbar \rightarrow 0$ limit of E_{xc} at fixed ρ

G.F., Cotar, Klueppelberg

Work in progress: leading order term. Novel functional form.

Thanks for attention!