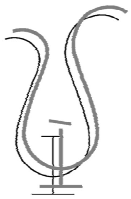
UNIVERSITY OF FLORIDA

Institute for Theory and Computation
in Molecular and Materials Sciences

Quantum Theory Project

Tutorial – 45th Sanibel Symposium
Plenary Sessions VII – XVII
(Tuesday – Friday)

So Hirata
Samuel B. Trickey
March 7, 2005



- The original Hohenberg-Kohn theorems of Density Functional Theory are

  Invertible mapping between external potential and density $V_{external} \leftrightarrow \rho$ (or n if you are a physicist)

  Universal variational functional of ρ alone for the ground state: $\min_\rho E[\rho] = E_0[\rho_0]$
- External magnetic fields are ignored (except later as a device to introduce spin-polarization)
- External magnetic fields introduce 2 issues: gauge invariance (roughly – avoid erroneous dependence on coordinate origins) & internal QM currents.

Vignale and Rasolt (Phys.Rev.Lett. **59**,2360 (1987); Phys. Rev. B **37**, 10695 (1988)) showed that Current Density Functional Theory needs to be in special form to be gauge invariant

- **Key variables** $n(\vec{r}) = \sum_k |\phi_k(\vec{r})|^2$ **and**

$$\vec{v}(\vec{r}) = \nabla \times \left(\frac{\vec{j}_p(\vec{r})}{n(\vec{r})}\right)$$

Vorticity = gauge-invariant composite variable

with $\vec{j}_p(\vec{r}) = \frac{\hbar}{2m_e i}\sum_k [\phi_k^*(\vec{r})\nabla\phi_k(\vec{r}) - c.c.]$ Paramagnetic QM current

- **Generalized Kohn-Sham structure**

$$\hat{h}\phi_k(\vec{r}) = \varepsilon_k\phi_k(\vec{r}) \qquad \hat{h} = \frac{1}{2m_e}\left[\frac{\hbar}{i}\nabla - \frac{e}{c}\vec{A}_{eff}(\vec{r})\right]^2 + V_{eff}(\vec{r})$$

$$V_{eff}(\vec{r}) = V_s(\vec{r}) + \frac{e^2}{2m_e c^2}[\vec{A}_{ext}^2(\vec{r}) - \vec{A}_{eff}^2(\vec{r})] \qquad V_{xc}(\vec{r}) = \frac{\delta E_{xc}[n(\vec{r}), \vec{j}_p(\vec{r})]}{\delta n(\vec{r})} \qquad V_H(\vec{r}) = e^2\int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|}d\vec{r}'$$

$$V_s(\vec{r}) = V_{ext}(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r}) \qquad \vec{A}_{eff}(\vec{r}) = \vec{A}_{ext}(\vec{r}) + \vec{A}_{xc}(\vec{r})$$

$$E_G = \sum_k \varepsilon_k - \frac{1}{2}\iint \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|}d\vec{r}d\vec{r}' + \tilde{E}_{xc}[n(\vec{r}), \vec{j}_p(\vec{r})] - \int [n(\vec{r})V_{xc}(\vec{r}) + \frac{e}{c}\vec{j}_p(\vec{r})\vec{A}_{xc}(\vec{r})]d\vec{r}$$

- K. Cappelle – Spin DFT has some non-uniqueness problems - $V_{external} \leftrightarrow \rho$ isn't always true. These are related to CDFT. A standard test of magnetic systems is the Heisenberg model, $H_{Heisenberg} = \sum_{i<j} J_{ij}\sigma_i \cdot \sigma_j$ a lattice of spins interacting pairwise.
- G. Vignale – CDFT has seen relatively little use compared to DFT. Review of the successes of CDFT with focus on the challenges – as with DFT, the challenge is the exchange-correlation quantities:

$$V_{xc}(\vec{r}) = \frac{\delta E_{xc}[n(\vec{r}), \vec{j}_p(\vec{r})]}{\delta n(\vec{r})} \qquad \vec{A}_{xc}(\vec{r})$$

Plenary VII Current Density Functional Theory (p. 4)

- S. Reimann-Wacker is co-author of a well-received review on quantum dots (Rev. Mod. Phys. **74**, 1283 (2002)). These are "artificial atoms", often with nearly 2D confinement. Their behavior in external magnetic fields is an important area of research. Unfortunately we have neither title nor abstract from her.

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Plenary VIII Dynamical Mean Field Theory (p. 1)

- The Kohn-Sham eigenvalues in DFT are guaranteed to have meaning only for the highest occupied one. This "I_p theorem" holds only for the exact E_{XC} . Customary approximations fail seriously: "the band gap problem".
- In solids with open *d* or *f* shell atoms as constituents the problem is particularly acute. These electrons are well-localized in narrow energy bands. That localization makes Coulomb correlations especially important. Physicists designate these as "strongly correlated" systems therefore.
- Standard DFT approximations handle strongly correlated systems poorly: metal oxide insulators are predicted to be metallic!
- DMFT addresses this problem by forthrightly separating the model one-electron states into atomic & itinerant ones.

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- The itinerant electron states are treated in KS DFT and provide a bath of levels ε_v for the atomic states.
- The atomic states are treated as a localized impurity in the bath.
- The hopping frequency of electrons into/out of that site is ω (essentially an impurity site electron affinity). The probability of hopping is measured by a local 1-body Green's function, G.
- The bath and site states are coupled by a hybridization matrix V_v
- The dynamical mean field $\Delta(\omega)$ and G are related self-consistently in a form very reminiscent of ordinary DFT.

[formulae next page]

• **Dynamical mean field:** $\Delta(\omega) = \sum_v \frac{|V_v|^2}{\omega - \varepsilon_v}$

• **Green's Function:** $G[\Delta\omega] = \sum_k \{\omega - \Sigma[\Delta(\omega)] - t_k\}^{-1}$

• **Self Energy:** $\Sigma[\Delta(\omega)] = \sum_k \Delta(\omega) - 1/G[\Delta(\omega)] + \omega$

• **Hopping matrix:** t_k

• **DMFT analogue to Hohenberg-Kohn-Sham functional**

$$E_{DMFT}[n(\vec{r}), G] = T_{DMFT}[n(\vec{r}), G] + \int n(\vec{r}) V_{ext}(\vec{r}) d\vec{r} + \frac{1}{2} \iint \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + \tilde{E}_{xc}[n(\vec{r}), G]$$

See G. Kotliar and D. Vollhardt, Physics Today, **57**, 53 (March 2004)

- Mark Jarrell is author of one of the key derivations in the development of DMFT and has made several applications. His talk is on extending the concept to a cluster of atoms with localized states rather than a single "impurity atom".
- Gabriel Kotliar is one of the original contributors to DMFT (see Physics Today article, previous slide). His talk will focus on two long-standing problems for ordinary DFT – the serious underestimate of the cell volume of δ-phase Plutonium and the peculiar behavior of the sequence of crystalline phases of Cerium (two fcc phases with volume difference of about 15% separated at low pressures by a hexagonal dhcp phase).

- Semi-empirical molecular orbital theory goes back at least to Extended Hückel Theory (EHT)

$$\sum_{\beta}\left(H_{\alpha\beta}-\varepsilon_i S_{\alpha\beta}\right)c_{i\beta}=0$$

$$H_{\alpha\beta}\approx S_{\alpha\beta}\left(H_{\alpha\alpha}+H_{\beta\beta}\right)/2$$

$$H_{\alpha\alpha}\approx I$$

- The labels refer to atomic orbitals χ_α This particular parametrization is the so-called Helmholtz-Wolfsberg prescription. The important conceptual point is that a molecular problem is reduced to a superposition of atomic parameters and an overlap matrix is all that must be computed.

• There are MANY other schemes for approximating the Hartree-Fock secular equation by parametrization weighted by overlap. For example "Complete Neglect of Differential Overlap"[*Approximate Molecular OrbitalTheory*, Pople and Beveridge, 1970 and refs.therein] chooses

$$\left\langle \alpha\beta \left| \frac{1}{r} \right| \mu\eta \right\rangle \approx \delta_{\alpha\beta}\delta_{\mu\eta} \left\langle \alpha\alpha \left| \frac{1}{r} \right| \mu\mu \right\rangle$$

as well as neglecting $S_{\alpha\beta}$ overlap.

• A key point is that the approximations must be invariant to spatial rotations of the molecule. In CNDO this is achieved by making all remaining 2-center integrals (atoms A, B) identical

$$\left\langle \alpha_A \alpha_A \left| \frac{1}{r} \right| \mu_B \mu_B \right\rangle = \gamma_{AB}$$

- Because semi-empirical methods are so fast, they continue to be appealing and useful. Among the major challenges for achieving greater realism are the possibilities of retaining subsets of exact matrix elements, improved parametrization schemes, etc. (A scheme that works for one class of chemically or physically interesting problems may not work for another class.)
- Edward Boudreaux has worked a long time on avoiding experimental inputs and scaling of parameters. Rather he attempts to get the parameters from computed atomic results. His particular favorite framework is modified EHT, with self-consistency.

- James Stewart was heavily involved in writing and parametrizing the well-known MOPAC series of codes associated with Michael Dewar. His talk is focused on a challenge just mentioned, namely to parametrize for study of a well-defined, significant problem class. His choice here is molecules of biochemical interest that are stable in water. The surprise result is that the calculations detected errors in published heats of formation!
- Henry Rzepa's talk illustrates another use of semi-empirical methods: find likely structures of complex molecules by using a parametrization that is designed to model structures well. Then use a more demanding method (here DFT) to study the details.

Electron Correlation Sessions – IX, XI, XII, XIV

Many sessions are concerned with **electron correlation** problems – sessions IX, XI, XII, XIV

Many-body problem in quantum mechanics

Classical mechanics	Quantum mechanics	Marriage & Family	Quantum field theory
0-body	0-body	0-body	0-body
1-body	1-body	1-body	1-body
2-body	2-body	2-body	2-body
3-body	3-body	3-body	3-body

Crudest physically acceptable approximate wave function may be:

Some assumed functional form

$$\underbrace{\Psi(1,2,\ldots,n)}_{\text{Fully coupled}} \approx A\underbrace{\left[\varphi_a(1)\varphi_b(2)\cdots\varphi_z(n)\right]}_{\text{Forced separation of variables}}$$

Orbital optimization

$$\Psi(1,2,\ldots,n) \approx A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right] \quad \text{SCF}$$

Variationally optimized

Approximate versus exact

$$\Psi(1,2,\ldots,n) \approx A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right] \quad \text{SCF = approx}$$

$$\Psi(1,2,\ldots,n) = c_0 A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right] \quad \text{Full CI = exact}$$

All excited-state Slater determinants

$$+c_1 A\left[\tilde{\varphi}_A(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right]$$
$$+c_2 A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_B(2)\cdots\tilde{\varphi}_z(n)\right]$$
$$+\ldots$$

Question 1: is this expansion exact? **YES**

Question 2: is this expansion rapidly converging? **NO**

$$\Psi(1,2,\ldots,n) = (99\%)A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right]$$

"Dynamical" electron correlation

$$+(0.6\%)A\left[\tilde{\varphi}_A(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right]$$
$$+(0.3\%)A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_B(2)\cdots\tilde{\varphi}_z(n)\right]$$
$$+\ldots$$

$$\Psi(1,2,\ldots,n) = (55\%)A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right]$$

"Non-dynamical" electron correlation

$$+(30\%)A\left[\tilde{\varphi}_A(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right]$$
$$+(10\%)A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_B(2)\cdots\tilde{\varphi}_z(n)\right]$$
$$+\ldots$$

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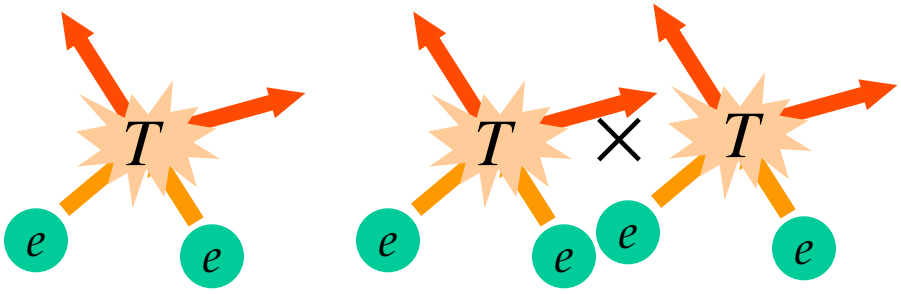
Electron Correlation Sessions – IX, XI, XII, XIV

$$\Psi(1,2,\ldots,n) = (99\%)A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right]$$

Dynamical electron correlation

$$+(0.6\%)A\left[\tilde{\varphi}_A(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right]$$
$$+(0.3\%)A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_B(2)\cdots\tilde{\varphi}_z(n)\right]$$
$$+(?\%)A\left[\tilde{\varphi}_A(1)\tilde{\varphi}_B(2)\cdots\tilde{\varphi}_z(n)\right]$$



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$$\Psi(1,2,\ldots,n) \approx 1\times A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right]$$
$$+T_A\times A\left[\tilde{\varphi}_A(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right]$$
$$+T_B\times A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_B(2)\cdots\tilde{\varphi}_z(n)\right]$$
$$+T_AT_B\times A\left[\tilde{\varphi}_A(1)\tilde{\varphi}_B(2)\cdots\tilde{\varphi}_z(n)\right]$$
$$=\left(1+\hat{T}+\tfrac{\hat{T}^2}{2!}+\tfrac{\hat{T}^3}{3!}+\ldots\right)A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right]$$
$$=\exp\left(\hat{T}\right)A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right] \quad \text{CC ansatz}$$

$$\Psi(1,2,\ldots,n) \approx \left(1+\hat{T}\right)A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right] \quad \text{CI ansatz}$$

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$$\Psi(1,2,\ldots,n) = (55\%)A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right]$$

Non-dynamical electron correlation:
$$+(30\%)A\left[\tilde{\varphi}_A(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right]$$
$$+(10\%)A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_B(2)\cdots\tilde{\varphi}_z(n)\right]$$
CI-type

Dynamical electron correlation:
$$+(0.6\%)A\left[\tilde{\varphi}_C(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right]$$
$$+(0.3\%)A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_D(2)\cdots\tilde{\varphi}_z(n)\right]$$
CC-type

Session XIV *Multi-reference CC & MBPT*
J. Paldus – State Universal Multi-reference Coupled-Cluster Method
J. Pittner – Multi-reference Brillouin-Wigner Coupled-Cluster Method

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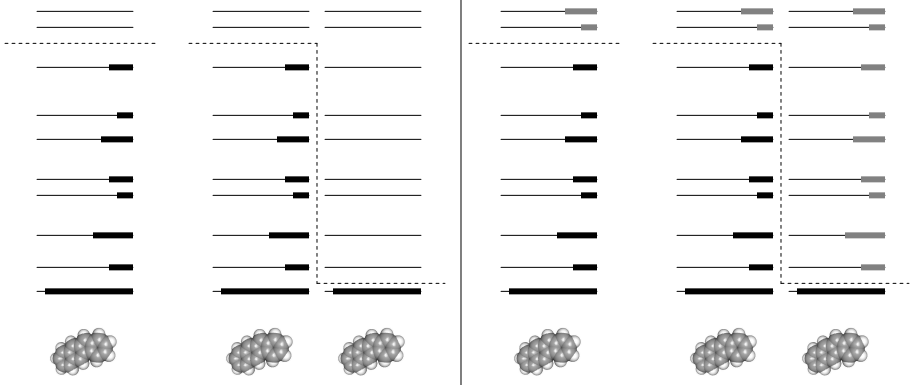
Not size-extensive

Size-extensive



Truncated CI

Truncated CC

Electron Correlation Sessions – IX, XI, XII, XIV

$$\Psi(1,2,\ldots,n) \approx \exp\left(\hat{T}\right)\Phi_{\mathrm{SCF}}$$ CC ansatz

How do we determine *T* amplitudes?

CCSD

$$\begin{cases} \left\langle \Phi_{\mathrm{SCF}} \left| \exp\left(\hat{T}\right) \right| \Phi_{\mathrm{SCF}} \right\rangle = E \\ \left\langle \Phi_i^a \left| \exp\left(\hat{T}\right) \right| \Phi_{\mathrm{SCF}} \right\rangle = 0 \\ \left\langle \Phi_{ij}^{ab} \left| \exp\left(\hat{T}\right) \right| \Phi_{\mathrm{SCF}} \right\rangle = 0 \end{cases}$$

Projection type equations

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CCSD

$$\left\langle \Phi_{\mathrm{SCF}} \left| \exp\left(\hat{T}\right) \right| \Phi_{\mathrm{SCF}} \right\rangle = E$$

$$\left\langle \Phi_i^a \left| \exp\left(\hat{T}\right) \right| \Phi_{\mathrm{SCF}} \right\rangle = 0$$

$$\left\langle \Phi_{ij}^{ab} \left| \exp\left(\hat{T}\right) \right| \Phi_{\mathrm{SCF}} \right\rangle = 0$$

CC moments

$$\left\langle \Phi_{ijk}^{abc} \left| \exp\left(\hat{T}\right) \right| \Phi_{\mathrm{SCF}} \right\rangle \neq 0$$

$$\left\langle \Phi_{ijkl}^{abcd} \left| \exp\left(\hat{T}\right) \right| \Phi_{\mathrm{SCF}} \right\rangle \neq 0$$

CC moments contain essential information about the difference between CC and full CI. Using them intelligently, we can improve upon plain CC theories.

Session XI *High-Level CC Theory*
K. Kowalski – Renormalized Coupled-Cluster Methods

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One of the five projection equations of CCSDTQ

Derivation & implementation of the CC approximations have been a nightmare!

Approximation	#Terms	#F77Lines	Year
CCD	11	3209	1978
CCSD	48	13213	1982
CCSDT	102	33932	1988
CCSDTQ	183	79901	1992

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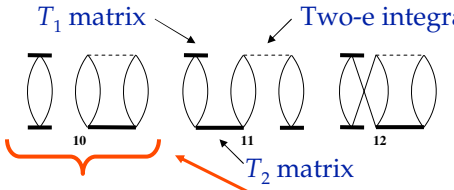
Not only arithmetic, but also the symbolic algebra (manipulation of determinants & diagrams) can be performed by computers, even on the fly!

Session XI *High-Level CC*
M. Kállay – Higher Excitations in Coupled-Cluster Theory
J. Olsen – Higher Excitations in CC, CI, PT

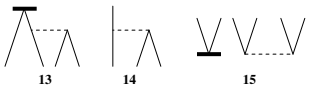
A diagram simply represents a product of matrices!

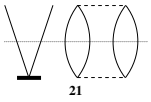
Closed diagrams usually are energies



Not size-extensive energy x energy?

Open diagrams represent operators





Unlinked diagrams inevitably violate size-extensivity

Approximate versus exact

$$\Psi(1,2,\ldots,n) \approx A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right]$$ SCF = approx

$$\Psi(1,2,\ldots,n) = c_0 A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right]$$ Full CI = exact

All excited-state Slater determinants

$$+c_1 A\left[\tilde{\varphi}_A(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right]$$
$$+c_2 A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_B(2)\cdots\tilde{\varphi}_z(n)\right]$$
$$+\ldots$$

Question 1: is this expansion exact? **YES**

Question 2: is this expansion rapidly converging? **NO**

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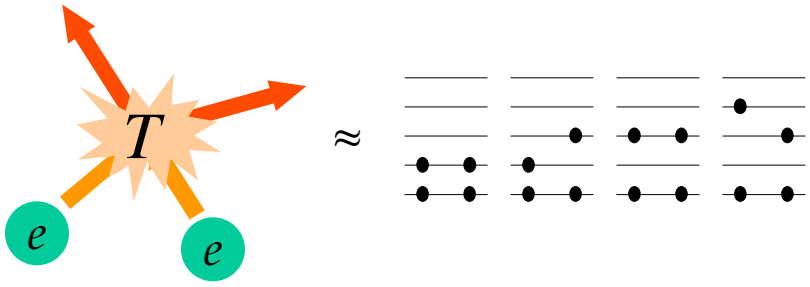
Full CI (or any approximation to it, such as CC, PT, etc.) describes *correlated motions* of electrons by including more and more *excited states*! This is not very appealing and, in fact, ***not very effective***.



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Electron Correlation Sessions – IX, XI, XII, XIV

$$\hat{H} = \sum\left(-\tfrac{1}{2}\nabla^2\right) - \sum\frac{Z}{r_{iA}} + \sum\frac{1}{r_{ij}}$$

Culprit

$$\Psi(1,2,\ldots,n) = c_0 A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right]$$
$$+c_1 A\left[\tilde{\varphi}_A(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right]$$
$$+c_2 A\left[\tilde{\varphi}_a(1)\tilde{\varphi}_B(2)\cdots\tilde{\varphi}_z(n)\right]+\ldots$$

$$\Psi(1,2,\ldots,n) = c_0 A\left[f(r_{ij})\tilde{\varphi}_a(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right]$$
$$+c_1 A\left[f(r_{ij})\tilde{\varphi}_A(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(n)\right]+\ldots$$

Other Correlated Approaches – IX, XII

$$\Psi = \exp\left[-\varsigma(r_1+r_2)\right]\left[c_1 + c_2 r_{12} + c_3(r_1 - r_2)\right]$$

Hylleraas' 3 term formula is as good as full CI with 7 zeta (19,200 determinants)

Session IX *High-Level Correlation*
F. Manby – Explicitly Correlated Electronic Structure

Session XII *Explicitly Correlated & Multi-resolution*
R. J. Harrison – Linear-Scaling Computational Chemistry Free of BSSE
K. Szalewicz – Gaussian Geminals
J. Noga – Coupled-Cluster R12 Theory
See also Session XVII *Clementi Celebration III*
W. A. Lester, Jr. – Quantum Monte Carlo

Other Correlated Approaches – IX, XII

Density Matrix Renormalization Group
(S.R. White Phys. Rev. B **48**, 10345 (1993))
Pick an optimal basis of size *m* by equivalent of diagonalizing the density matrix in a larger set and keeping fns with the *m* largest eigenvalues. Originally for statistical mechanical problems.

Session IX *High-Level Correlation*

S.R. White – *The Density Matrix Renormalization Group*
Review of the method, applications to quantum chemistry, particularly to localization of orbitals

T. Van Voorhis – *Fixed-charge Density Functional Theory*
Think of the density not as dependent on the nuclear framework but as fixed for various subsystems– the "driver" of the system – and explore consequences.

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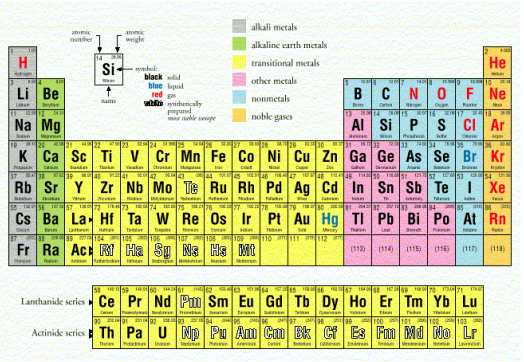
Relativistic Quantum Chemistry

The basic equation of motion of chemistry is quantum mechanics (Schrödinger equation)
… and special theory of relativity (Dirac equation)!



Relativity negligible

Relativity ≈ correlation

Relativity > correlation
Schrödinger equation
will break down!

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Relativistic effects: increase in electron effective mass → contraction of inner core *s* and *p* orbitals → increased shielding → expansion of *d* and *f* orbitals → changes in bond lengths, vibrational frequencies, bond energies, etc.

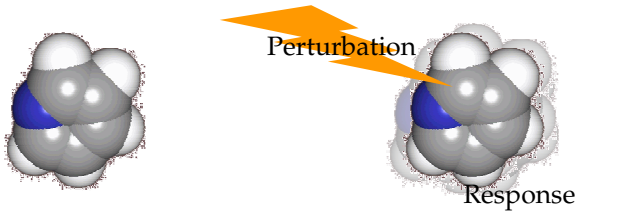
Relativistic effects: spin-orbit interaction → spectroscopic fine structures, inter-system crossing, phosphorescence, single molecule magnets, etc.

Four-component: α and β, electrons and positrons coupled
Two-component: α and β electrons coupled
One-component, ECP: scalar relativistic effects only

Complex spinors versus real orbitals
Variational collapse versus variational stability
Double group versus point group
Kramer's pair versus α and β electron pair

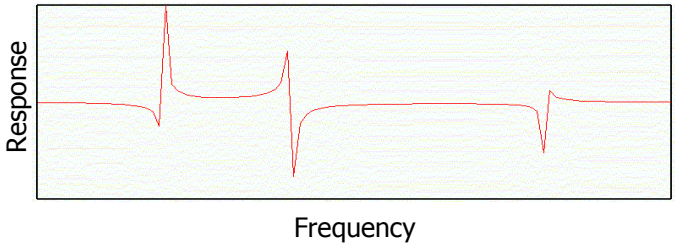
Session XIII *Relativistic Quantum Mechanics*
L. Visscher – Four-Component Relativistic Methods
T. Nakajima – Four- and Two-Components HF and DFT
J. Li – Computational Actinide Chemistry
See also Session XVI *Clementi Celebration II*
A. Strich – Effects of Spin-Orbit Coupling on Electronic Transitions in Transition Metal Complexes

Interaction Between Light and Matter



$$\hat{H} = \sum\left(-\tfrac{1}{2}\nabla^2\right) - \sum\frac{Z}{r_{iA}} + \sum\frac{1}{r_{ij}}$$

$$\hat{H}' = \hat{H} + \Delta\exp(i\omega t)$$



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Interaction Between Light and Matter

Density Functional Theory			Molecular Orbital Theory		
Tamm-Dancoff TD-TDDFT	Linear response TDDFT	Local functional	Hartree-Fock Theory	Linear response TDHF	Tamm-Dancoff CIS
		Gradient-corrected			
		Hybrid HF functional			
Tamm-Dancoff TD-TDOEP	Linear response TDOEP	Optimized Effective Potential	CC2 CC3 CC4 ...	EOM-CC2 EOM-CC3 EOM-CC4 ...	

Exact solution

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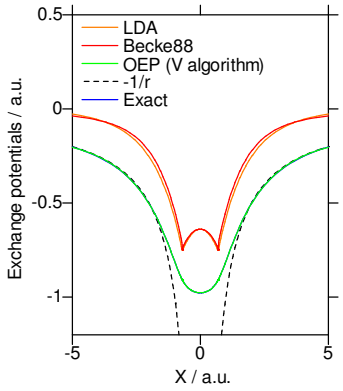

Rydberg excited states
Charge-transfer excited states
Ionization potentials
Size-extensivity

Session IX *High-Level Electron Correlation*
T. Van Voorhis – Fixed Charge DFT; may be TDDFT?
See also Session XVI *Clementi Celebration II*
A. Rizzo – Non Linear Mixed Electric and Magnetic Properties

This time-dependent perturbation theory approach is not adequate for *intense* radiation fields. Such fields are ***not*** a perturbation and higher-order responses are expected.

Rather, time-dependent wave functions should be expanded by the exact solutions of the time-dependent Schrödinger equation.

Floquet states are such a basis (solutions of time-periodic Hamiltonian).

Session XIV *Multi-reference CC & MBPT*
M. Hoffmann – Accurate Electronic Structure in Intense Radiation Fields