

Methods of the 21st century

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Introduction

What we have:

- Exact non-relativistic Hamiltonian, Full-CI in a given basis set
- Full CI too expensive: two possible issues:
 - Either one reference and sophisticated correlation
 - Or several important reference states and simple correlation
- All contained in the Full CI model

Beyond the Full CI model:

- Density Functional theory
 - Explicitly correlated methods
 - Quantum Monte Carlo
- Additional freedom and weaker (no?) basis set dependence

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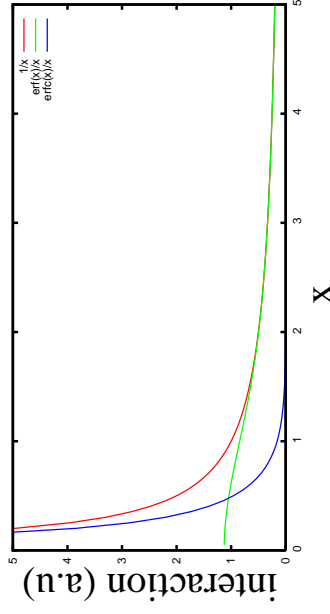
Range-separated density-functional theory

DFT good for dynamical correlation, but fails for long-range interactions

Basic idea:

- Use DFT for short-range electron-electron interactions
- Use MP2 or CCSD(T) for long-range correlation effects

Electron-electron interaction: $\frac{1}{r_{ij}} = \frac{\text{erf}(\mu r_{ij})}{r_{ij}} + \frac{\text{erfc}(\mu r_{ij})}{r_{ij}}$



Range-separated density-functional theory

Common Kohn-Sham procedure: minimize

$$E_{\text{exact}} = \min_{\Phi} \{ \langle \Phi | T + V_{\text{ne}} | \Phi \rangle + E_{\text{HXC}}[n_{\Phi}] \}$$

- HXC=Hartree-Exchange-Correlation functional

Range-separated *hybrid* (RSH) scheme

$$E^{\text{RSH}} = \min_{\Phi} \{ \langle \Phi | T + V_{\text{ne}} + W_{\text{ee}}^{\text{lr}} | \Phi \rangle + E_{\text{HXC}}^{\text{sr}}[n_{\Phi}] \}$$

Long-range part $\langle \Phi | W_{\text{ee}}^{\text{lr}} | \Phi \rangle$:

Hartree term (electrostatic interaction) and Hartree-Fock (HF) exchange. Kohn-Sham-like RSH equations

$$(T + V_{\text{ne}} + V_{\text{H}} + V_{\text{X}}^{\text{lr}} + V_{\text{XC}}^{\text{sr}} | \phi_i^{\text{RSH}} \rangle = \epsilon_i | \phi_i^{\text{RSH}} \rangle$$

- V_{X}^{lr} : non-local HF exchange potential, but with “erf” part $1/r_{ij}$
- μ -adapted functionals
- Convergence: orbitals $|\phi_i^{\text{RSH}}\rangle$ and orbital energies ϵ_i

The long-range correlation part

- No long-range **correlation** part yet, excluded from RSH equations
- $E_{\text{Corr}}^{\text{lr}}$ responsible for dispersion forces

Second-order perturbation Møller-Plesset theory

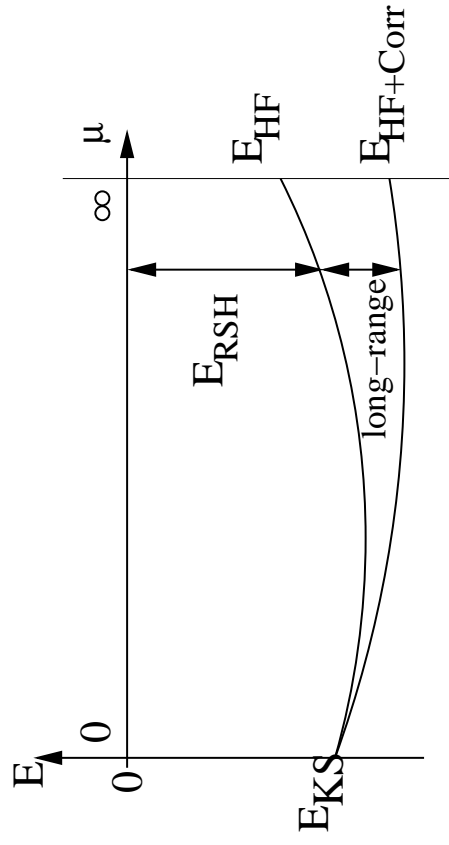
$$E_{\text{Corr}}^{\text{lr}}(\text{MP2}) = \sum_{ijab} \frac{[2(i a | j b) - (i b | j a)](i a | j b)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

- long-range bi-electronic integrals (the “erf” part) over the RSH orbitals ϕ
- Diagonal Fock matrix elements ϵ of the RSH step
- All quantities (integrals and denominators) depend on the separation parameter μ
- Use CCSD(T) as long-range correlation

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The long-range correlation part



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Performance

VAN DER WAALS FORCES IN DENSITY FUNCTIONAL...

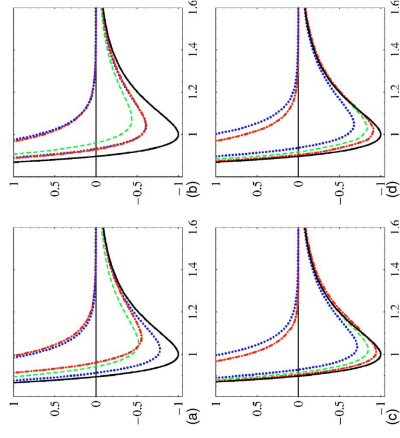
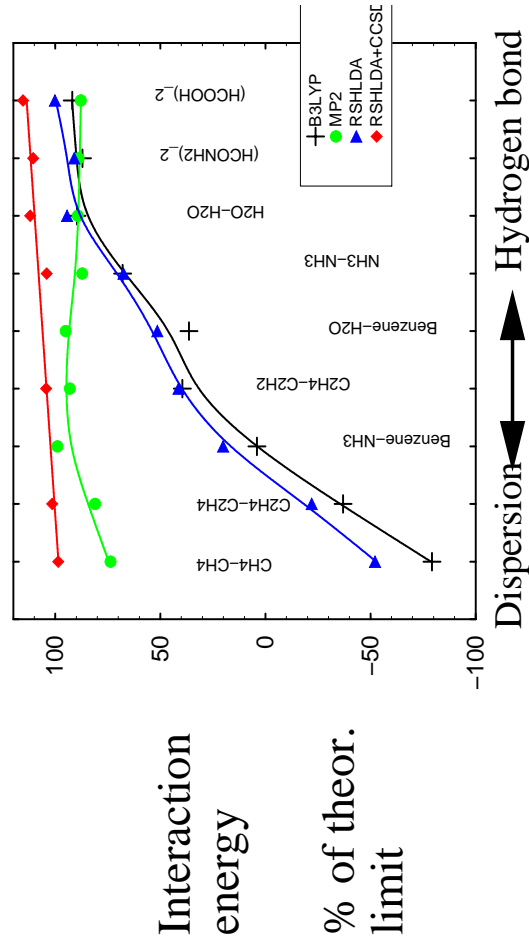


FIG. 1. (Color online) Reduced HF (dotted repulsive), RSH (dotted-dashed repulsive), MP2 (dotted), CCSD(T) (dashed), RSH+MP2 (dotted-dashed), and Tang-Toennies reference (full) potential curves for (a) He₂, (b) Ne₂, (c) Ar₂, and (d) Kr₂ dimers.

J.G.Ángyán, I.C.Gerber, A.Savin, *J.Toulouse, Phys.Rev., A72 (2005) 12510*

Performance



Interaction energy

% of theor. limit

Dispersion ← → Hydrogen bond

Explicitly correlated methods

T.Kato (1957): Ψ linear in r_{12} for small r_{12}

$$\lim_{r_{12} \rightarrow 0} \left(\frac{\partial \Psi}{\partial r_{12}} \right)_{av} = \frac{1}{2} \Psi(r_{12} = 0)$$

Ansatz (W.Kutzelnigg, W.Klopper 1990): $\Psi = \frac{1}{2} r_{12} \Phi_{HF}$

- Define Hamiltonian $\hat{H} = E_0 + \hat{H}^{(1)} + \hat{H}^{(2)}$
- Define excited determinants

$$\Phi_{ij}^a = a_a^\dagger a_i \Phi_0 \quad \Phi_{ij}^{ab} = a_a^\dagger a_b^\dagger a_i a_j \Phi_0$$

and contracted excitations

$$\Phi_{ij} = \frac{1}{2} \sum_{\alpha\beta} \langle \phi_\alpha \phi_\beta | r_{12} | \phi_i \phi_j \rangle \Phi_{ij}^{\alpha\beta}$$

- Construct all matrix elements in the parts of the Hamiltonian and the determinants.

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Explicitly correlated methods

Technical problem: 3- and 4-electron integrals

$$\begin{aligned} & \langle \phi_a(1) \phi_b(2) \phi_c(3) | r_{12} \frac{1}{r_{23}} | \phi_e(1) \phi_f(2) \phi_g(3) \rangle \\ & \langle \phi_a \phi_b \phi_c \phi_d | r_{12} \frac{1}{r_{34}} | \phi_e \phi_f \phi_g \phi_h \rangle \end{aligned}$$

Solved by introduction of the “Resolution of the identity” $1 = \sum_\alpha | \phi_\alpha \rangle \langle \phi_\alpha |$

$$\begin{aligned} & \iint \iint \phi_a(1) \phi_b(2) \phi_c(3) r_{12} \frac{1}{r_{23}} \phi_e(1) \phi_f(2) \phi_g(3) d^3 r_1 d^3 r_2 d^3 r_3 \\ & = \iint \iint \phi_a(1) \phi_b(2) r_{12} \phi_e(1) \phi_c(3) \frac{1}{r_{23}} \phi_f(2) \phi_g(3) d^3 r_1 d^3 r_2 d^3 r_3 \\ & = \sum_\alpha \langle \phi_a \phi_b | r_{12} | \phi_e \phi_\alpha \rangle \langle \phi_\alpha \phi_c | \frac{1}{r_{23}} | \phi_f \phi_g \rangle \end{aligned}$$

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Explicitly correlated methods

W.Klopper, C.C.M.Samson, J.Chem.Phys., **116** (2002) 6397

Vol. 116, No. 15, 15 April 2002

MP2-R12 methods

TABLE II. All-electron Møller–Plesset second-order energies ($E^{(2)}$ in m E_h) of the Ne atom.

Basis ^a	MP2 ^b	Original method			New Ansatz 1			New Ansatz 2		
		R12/A'	R12/B	R12/A'	R12/A'	R12/B	R12/A'	R12/B	R12/A'	R12/B
<i>sp</i>	-191.99	-688.49	-506.95	-361.84	-330.37	-362.45	-331.33			
<i>spd</i>	-322.27	-408.78	-395.11	-361.97	-358.19	-390.71	-382.59			
<i>spdf</i>	-359.84	-389.71	-387.19	-376.20	-375.30	-389.76	-387.49			
<i>spdf g</i>	-374.12	-388.62	-387.89	-383.27	-382.95	-388.67	-387.99			
<i>spdf gh</i>	-379.46	-388.29	-388.01	-386.13	-385.97	-388.35	-388.07			
<i>spdf ghi</i>	-381.65	-388.19	-388.04	-387.69	-387.56	-388.24	-388.09			

^aSubsets of the 20s14p11d9f7g5h3i basis. The 32s24p18d15f12g9h6i basis was applied as an auxiliary basis in all calculations.

^bConventional all-electron MP2 energy.

Much faster convergence of the correlation energy with ℓ

Explicitly correlated methods

Recent developments: H.-J.Werner, T.B.Adler, F.R.Manby, J.Chem.Phys., **126** (2007) 164102

$$|\Phi_{ij}^{kl}\rangle = \sum_{\alpha\beta} |\Phi_{ij}^{\alpha\beta}\rangle F_{\alpha\beta}^{kl}$$

$$F_{\alpha\beta}^{kl} = \langle kl | \hat{F}_{12} \hat{Q}_{12} | \alpha\beta \rangle \quad \hat{F}_{12} = e^{-\beta r_{12}}$$

- \hat{Q} projector to keep determinants and WFs orthogonal.
- Localized orbitals \rightarrow less integrals
- Coupled-Cluster expansion
- Density fitting: $\rho(\vec{r}) \approx \sum_i c_i \chi_i(\vec{r})$

Quantum Monte Carlo method

Consider a wavefunction

$$\Psi(\vec{r}_1, \vec{r}_2, \dots) = e^{f(r_{ee}) + f(r_{en}) + f(r_{een})} \Phi_{HF}$$

Try again to calculate $E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$

Impossible! Integrals far too complicated.

Radically different approach:

Sample the 3N-dimensional integral with random electron positions

$$\begin{aligned} E &= \int \dots \int \Psi(\vec{r}_1 \dots \vec{r}_n) \hat{H} \Psi(\vec{r}_1 \dots \vec{r}_n) d^3r_1 \dots d^3r_n \\ &= \int \dots \int \underbrace{\Psi^2(\vec{r}_1 \dots \vec{r}_n)}_{\text{weight}} \underbrace{\frac{\hat{H} \Psi(\vec{r}_1 \dots \vec{r}_n)}{\Psi(\vec{r}_1 \dots \vec{r}_n)}}_{\text{local energy}} d^3r_1 \dots d^3r_n \\ &\longrightarrow \frac{1}{N_{\text{conf}}} \sum_{\text{configurations}} \hat{H} \Psi(\vec{r}_1 \dots \vec{r}_n) \frac{1}{\Psi(\vec{r}_1 \dots \vec{r}_n)} \end{aligned}$$

Quantum Monte Carlo method

Jastrow factor:

$$\begin{aligned} f(r_{ee}) &= \frac{1}{2} \left(\frac{r_{ij}}{1 + br_{ij}} \right) \\ f(r_{ne}) &= -Z_\alpha \left(\frac{r_{i\alpha}}{1 + br_{i\alpha}} \right) \end{aligned}$$

$$\Psi(\vec{r}_1, \dots, \vec{r}_n) = e^{f(r_{ee})} e^{f(r_{ne})} e^{f(r_{een})} \Phi_0$$

Optimize parameters of the Jastrow factor

- Run as long as you want
- Generation of configurations: move electrons in real space
- Metropolis algorithm: $P(a \rightarrow b) \sim \exp(-\Delta E_{a \rightarrow b})$
- Not only energy but as well statistical error bars !

Computationally VERY HEAVY

Quantum Monte Carlo method

Diffusion Monte Carlo:

$$i \frac{\partial \Psi(\vec{r}, t)}{\partial t} = \hat{H} \Psi(\vec{r}, t)$$

Evolution in imaginary time $t \rightarrow i\tau$

$$-\frac{\partial \Psi(\vec{r}, \tau)}{\partial \tau} = \hat{H} \Psi(\vec{r}, \tau)$$

Subtract the exact (unknown) ground state energy E_0 . Any Ψ is a sum over eigenstates of \hat{H} : $\Psi = \sum_I c_I \Psi_I$

$$-\frac{\partial \Psi(\vec{r}, \tau)}{\partial \tau} (\hat{H} - E_0) \Psi = \sum_I c_I (E_I - E_0) \Psi_I$$

All go exponentially to zero, but Ψ_0 .

Quantum Monte Carlo method

Procedure:

- Initial configurations
- Move in a time step $\Delta\tau$
- Replicate or delete configurations according to

$$[W(X)] = \exp(-\Delta\tau(V(X) - E_T)) + z$$

with random number z

- Renormalize number of configurations to maintain a fixed number

Configurations will reproduce in the infinite limit the ground state wavefunction Ψ_0 .

- Reference data
- Homogeneous electron gas
