Methods of the 21st century

Peter Reinhardt

Laboratoire de Chimie Théorique, Université Paris VI, 75252 Paris CEDEX 05,
Peter.Reinhardt@upmc.fr

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
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
\[
E^{\text{RSH}} = \min_{\Phi} \{ \langle \Phi | T + V_{\text{ne}} + W^X_{\text{HF}} | \Phi \rangle + E_{\text{HXC}}^{\text{eff}} [n_{\Phi}] \}
\]

Long-range part \( \langle \Phi | W^X_{\text{HF}} | \Phi \rangle \):
- Hartree term (electrostatic interaction) and Hartree-Fock (HF) exchange.

Kohn-Sham-like RSH equations
\[
(T + V_{\text{ne}} + V_H + V^X_{\text{HF}} + V^X_{\text{XC}}) | \phi_i^{\text{RSH}} \rangle = \epsilon_i | \phi_i^{\text{RSH}} \rangle
\]
- \( V^X_{\text{HF}} \): non-local HF exchange potential, but with “erf” part \( 1/r_{ij} \)
- \( \mu \)-adapted functionals
- Convergence: orbitals \( | \phi_i^{\text{RSH}} \rangle \) and orbital energies \( \epsilon_i \)
The long-range correlation part

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

Second-order perturbation Møller-Plesset theory

$$E_{\text{Corr}}^L (\text{MP2}) = \sum_{ijab} \frac{2(ia|jb) - (ib|ja)(ia|jb)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

- long-range bi-electronic integrals (the “erf” part) over the RSH orbitals $\phi$
- Diagonal Fock matrix elements $\epsilon$ of the RSH step
- All quantities (integrals and denominators) depend on the separation parameter $\mu$
- Use CCSD(T) as long-range correlation
Interaction energy

% of theor. limit

Displacement

Hydrogen bond

FIG. 1. (Color online) Reduced HF (dotted repulsive), RSH (dotted-dashed repulsive), MP2 (dotted), CCSD(T) (dashed), RSH + MP2 (dotted-dashed), and Tan-Toennies reference (full) potential curves for (a) H2C, (b) N2C, (c) ArC, and (d) Kr dimers.

Explicitely correlated methods

T.Kato (1957): $\Psi$ linear in $r_{12}$ for small $r_{12}$

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

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

$$\Phi^a_i = a_i^\dagger a_i \Phi_0$$

$$\Phi^{ab}_{ij} = a_i^\dagger a_j a_i a_j \Phi_0$$

and contracted excitations

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

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

Explicitely correlated methods

Technical problem: 3- and 4-electron integrals

$$\langle \phi_a(1) \phi_b(2) \phi_c(3) | r_{12} \frac{1}{r_{23}} | \phi_e(1) \phi_f(2) \phi_g(3) \rangle$$

$$\langle \phi_a \phi_b \phi_c \phi_d | r_{12} \frac{1}{r_{34}} | \phi_e \phi_f \phi_g \phi_h \rangle$$

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


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

\[ F_{\alpha \beta}^{kl} = \langle k l | \hat{F}_{12} \hat{Q}_{12} | \alpha \beta \rangle \]

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

\[ \rho(\vec{r}) \approx \sum_i e_i \chi_i(\vec{r}) \]

- Subset of the 20x14p11d9f7g5h3i basis. The 32x24p18d15f12g8h6i basis was applied as an auxiliary basis in all calculations.
- Conventional all-electron MP2 energy.
Performance

Fig. 1 Interaction potentials for the Ne-dimer.


Performance

Fig. 4 Errors of the total MP2 interaction energies for the AVQZ and AVSZ basis sets and of the MP2-F12(D)/AVTZ (β = 1.0Å⁻¹) results relative to the MP2/CBS[45] estimates of the basis set limits.

Quantum Monte Carlo method

Consider a wavefunction
\[ \Psi(\vec{r}_1, \vec{r}_2, \ldots) = e^{f(r_{ee}) + f(r_{en}) + f(r_{een})} \Phi_{HF} \]

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
\[ E = \int \ldots \int \Psi(\vec{r}_1, \ldots, \vec{r}_n) \hat{H} \Psi(\vec{r}_1, \ldots, \vec{r}_n) d^3r_1 \ldots d^3r_n \]
\[ = \int \ldots \int \Psi^2(\vec{r}_1, \ldots, \vec{r}_n) \frac{\hat{H} \Psi(\vec{r}_1, \ldots, \vec{r}_n)}{\Psi(\vec{r}_1, \ldots, \vec{r}_n)} d^3r_1 \ldots d^3r_n \]
\[ \rightarrow \frac{1}{N_{\text{conf}}} \sum_{\text{configurations}} \frac{\hat{H} \Psi(\vec{r}_1, \ldots, \vec{r}_n)}{\Psi(\vec{r}_1, \ldots, \vec{r}_n)} \]

Quantum Monte Carlo method

Jastrow factor:
\[ f(r_{ee}) = \frac{1}{2} \left( \frac{r_{ij}}{1 + br_{ij}} \right) \]
\[ f(r_{ne}) = -Z_a \left( \frac{r_{ia}}{1 + br_{ia}} \right) \]
\[ \Psi(\vec{r}_1, \ldots, \vec{r}_n) = e^{f(r_{ee})} e^{f(r_{en})} e^{f(r_{een})} \Phi_0 \]

Optimize parameters of the Jastrow factor
- Run as long as you want
- Generation of configurations: move electrons in real space
- Metropolis algorithm: \( P(a \rightarrow b) \sim \exp(-\Delta E_a - b) \)
- Not only energy but as well statistical error bars!

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 \( \Psi \) is a sum over eigenstates of \( \hat{H} \): \( \Psi = \sum c_I \psi_I \)
\[ -\frac{\partial \Psi(\vec{r}, \tau)}{\partial \tau} \left( \hat{H} - E_0 \right) \Psi = \sum c_I (E_I - E_0) \psi_I \]

All go exponentially to zero, but \( \psi_0 \).

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 \( \psi_0 \).
- Reference data
- Homogeneous electron gas

Computationally VERY HEAVY