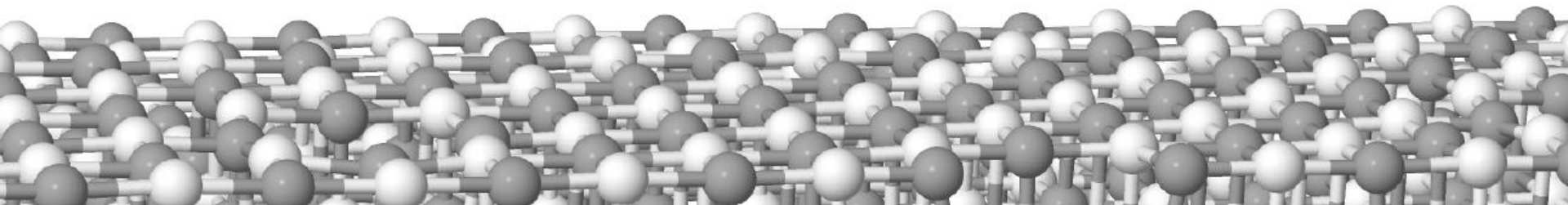


Beyond DFT for extended systems

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Outline

- **DFT versus wave function methods**
- **Electron repulsion integrals and resolution of identity**
- **Beyond DFT methods for extended (periodic) systems**
- **Conclusions**

DFT versus wave function methods

Ground-state electronic structure problem

$$\left[-\frac{1}{2} \sum_i \frac{\partial^2}{\partial \mathbf{r}_i^2} - \sum_i \sum_J \frac{Z_J}{|\mathbf{r}_i - \mathbf{R}_J|} + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + V^{\text{ext}}(\{\mathbf{r}_i\}) \right] \Psi(\{\mathbf{r}_i\}, \{\sigma_i\}) = E \Psi(\{\mathbf{r}_i\}, \{\sigma_i\})$$

$\Psi(\{\mathbf{r}_i\}, \{\sigma_i\})$ – many-body wave function, depends on spatial (\mathbf{r}_i) and spin (σ_i) coordinates of particles (also on nuclear coordinates (\mathbf{R}_J) and $V^{\text{ext}}(\{\mathbf{r}_i\})$)

- already include approximations (Born-Oppenheimer, non-relativistic, no spin-orbit coupling, no magnetic field)
- wave function depends on $4N$ variables (spatial + spin)
- electrons interact via Coulomb forces

Non-interacting fermions

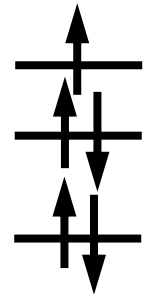
$$\hat{H} = -\frac{1}{2} \sum_i \frac{\partial^2}{\partial \mathbf{r}_i^2} - \sum_i \sum_J \frac{Z_J}{|\mathbf{r}_i - \mathbf{R}_J|} + \cancel{\sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}} + \frac{V^{\text{ext}}(\{\mathbf{r}_i\})}{}$$



$$V^{\text{ext}}(\{\mathbf{r}_i\}) = \sum_i v(\mathbf{r}_i)$$

$$\Psi(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N) = \frac{1}{\sqrt{N!}} \det|\psi_1(\mathbf{r}_1, \sigma_1), \dots, \psi_N(\mathbf{r}_N, \sigma_N)|$$

one-particle states



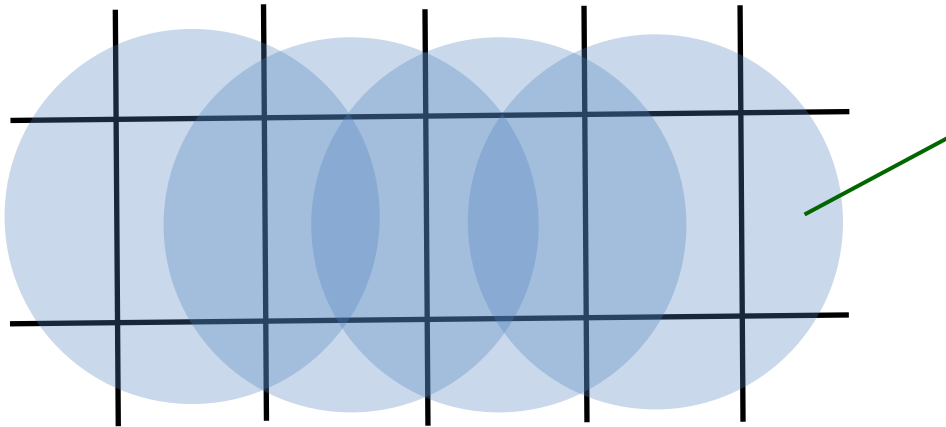
$$\left(-\frac{1}{2} \frac{\partial^2}{\partial \mathbf{r}^2} - \sum_J \frac{Z_J}{|\mathbf{r} - \mathbf{R}_J|} + v(\mathbf{r}) \right) \psi_n(\mathbf{r}) = \varepsilon_n \psi_n(\mathbf{r}),$$

From reciprocal to real space

$$w_{n\mathbf{R}}(\mathbf{r}) = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{R}} \sum_m U_{nm}^{(\mathbf{k})} \psi_{m\mathbf{k}}(\mathbf{r})$$

Wannier functions: not unique, can be chosen more or less localized

An arbitrary unitary transformation within occupied and virtual subspaces



Wannier functions in each unit cell

$$\Psi = \frac{1}{\sqrt{N!}} \det |w_{1\mathbf{R}_1}(\mathbf{r}_1) \dots w_{N\mathbf{R}_1}(\mathbf{r}_N) \dots|$$

Interacting fermions (electrons)

$$\hat{H} = -\frac{1}{2} \sum_i \frac{\partial^2}{\partial \mathbf{r}_i^2} - \sum_i \sum_J \frac{Z_J}{|\mathbf{r}_i - \mathbf{R}_J|} + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\Psi(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N) \approx \frac{1}{\sqrt{N!}} \det|\psi_1(\mathbf{r}_1, \sigma_1), \dots, \psi_N(\mathbf{r}_N, \sigma_N)|$$



variational principle

$$\min_{\psi_i} \langle \Psi | \hat{H} | \Psi \rangle \Rightarrow \frac{\delta \langle \Psi | \hat{H} | \Psi \rangle}{\delta \psi_i} = 0$$

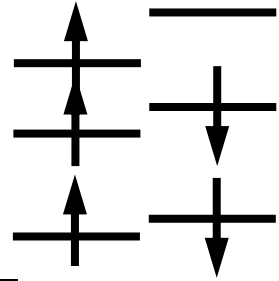
Introduce basis set: $\psi_i(\mathbf{r}, \sigma) = s(\sigma) \sum_j c_{ij}^\sigma \varphi_j(\mathbf{r}), \frac{\partial \langle \Psi | \hat{H} | \Psi \rangle}{\partial c_{ij}} = 0$

The Hartree-Fock (HF) approximation

$$\Psi(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N) \approx \frac{1}{\sqrt{N!}} \det|\psi_1(\mathbf{r}_1, \sigma_1), \dots, \psi_N(\mathbf{r}_N, \sigma_N)|$$

$$E_{\text{tot}} = \sum_{n=1}^N \langle \psi_n | \hat{h} | \psi_n \rangle + \frac{1}{2} \sum_{I=1}^M \sum_{J=1}^M \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' -$$

$$- \frac{1}{2} \sum_{m,n=1}^N \int \frac{\psi_m^*(\mathbf{r}, \sigma) \psi_n(\mathbf{r}, \sigma) \psi_n^*(\mathbf{r}', \sigma') \psi_m(\mathbf{r}', \sigma')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' d\sigma d\sigma'$$

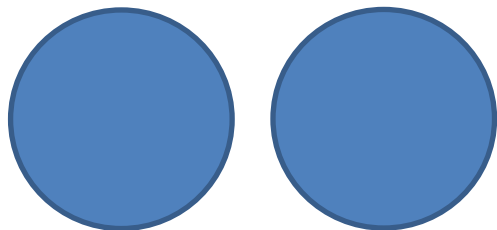


HF (exact) exchange energy

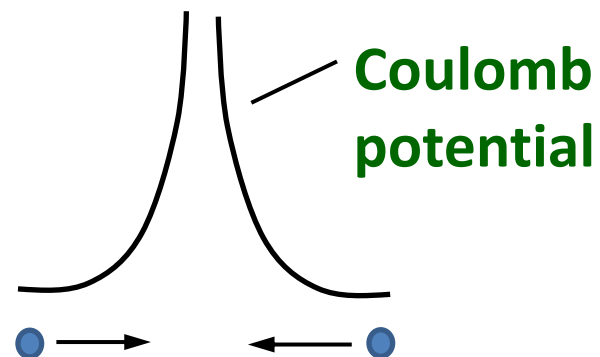
- No self-interaction
- Coulomb mean-field → no dynamic correlation, single determinant → no static correlation

The Hartree-Fock (HF) approximation

Dynamic correlation:

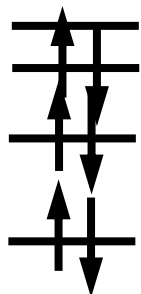


versus

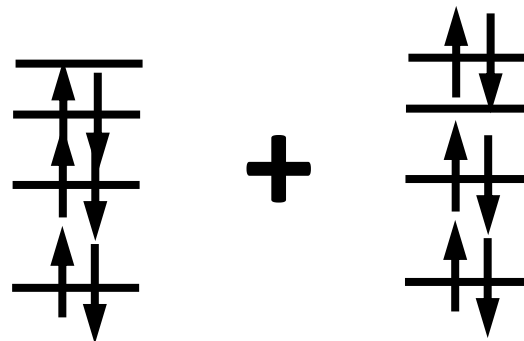


smaller e density, large $\partial\psi / \partial\mathbf{r}$

Non-dynamic (static) correlation:



versus

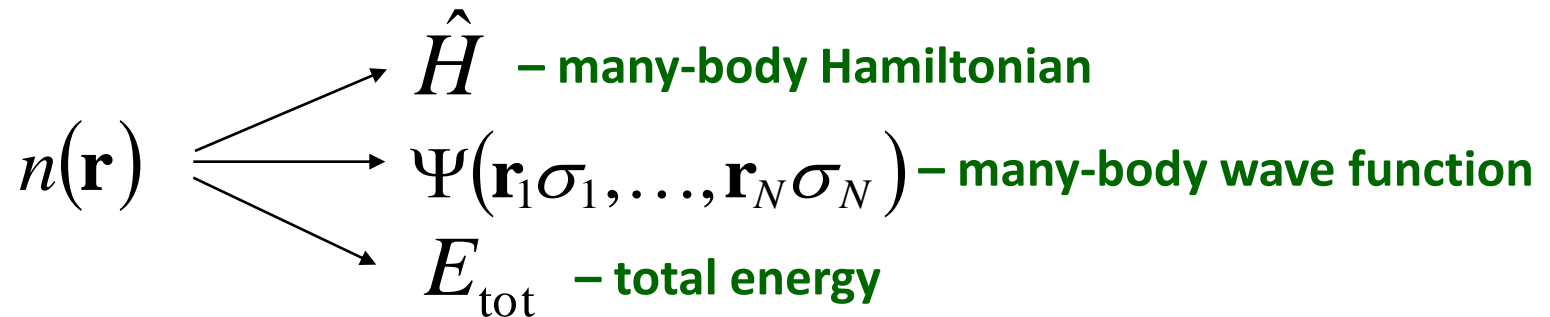


(quasi)degenerate HOMO-LUMO)

HF approximation \rightarrow $\geq 90\%$ of total energy, overestimates ionicity

Density functional theory

Density functional theory: Hohenberg-Kohn theorem



$$E_{\text{tot}} = T[n] - \sum_{I=1}^M Z_I \int \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_I|} d^3r + \frac{1}{2} \sum_{I=1}^M \sum_{J=1}^M \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + E_{\text{XC}}[n]$$

Approximations to $E_{\text{XC}}[n]$: Local density approximation (LDA), generalized gradient approximation (GGA), meta-GGA

Standard DFT and the self-interaction error

$$E_{\text{tot}} = T[n] - \sum_{I=1}^M Z_I \int \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_I|} d^3 r + \frac{1}{2} \sum_{I=1}^M \sum_{J=1}^M \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r' + E_{\text{XC}}[n]$$

$n(\mathbf{r})$ -- electron density

(includes self-interaction)

exchange-correlation (XC) energy

LDA, GGA, meta-GGA: $E_{\text{XC}}[n] = E_{\text{X}}^{\text{loc}}[n] + E_{\text{C}}^{\text{loc}}[n]$

Standard DFT: (Semi)local XC operator → low computational cost

Removing self-interaction + preserving fundamental properties (e.g., invariance with respect to subspace rotations) is non-trivial → residual self-interaction (error) in standard DFT

**Consequences of self-interaction (no cancellation of errors):
localization/delocalization errors, incorrect level alignment (charge transfer, reactivity, etc.)**

Hybrid DFT

$$E_{\text{XC}}[\{\psi\}] = \alpha E_{\text{X}}^{\text{HF}}[\{\psi\}] + (1 - \alpha) E_{\text{X}}^{\text{loc}}[n] + E_{\text{C}}^{\text{loc}}[n]$$

-- easy in Kohn-Sham formalism ($n = \sum_n f_n |\psi_n|^2$)

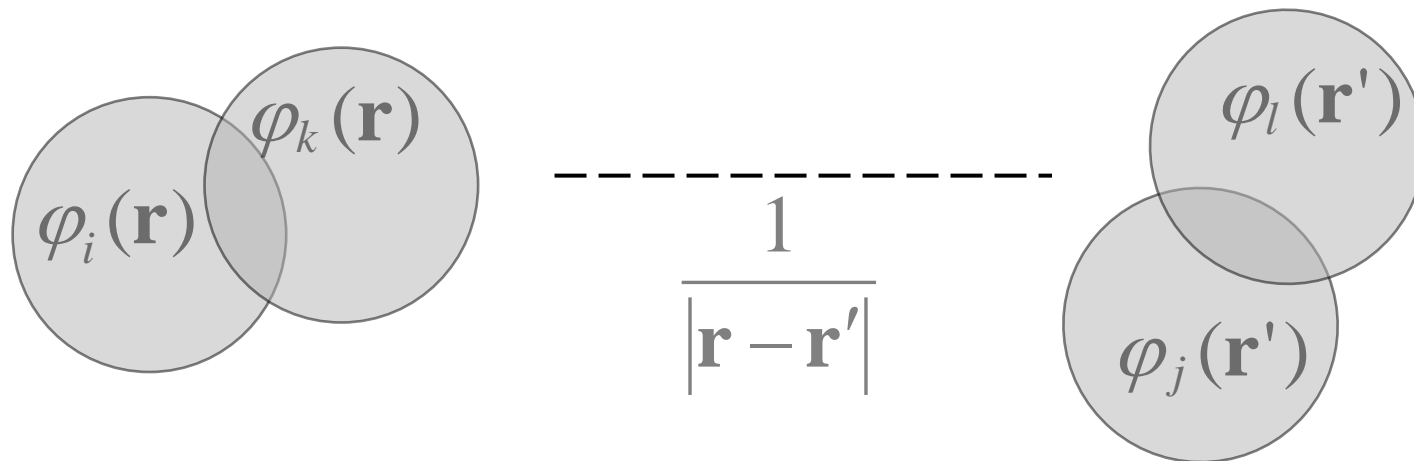
Perdew, Ernzerhof, Burke (J. Chem. Phys. 105, 9982 (1996)): $\alpha = 1/N$

MP4 $\rightarrow N = 4$, but “An ideal hybrid would be sophisticated enough to optimize N for each system and property.”

$$E_{\text{XC}}^{\text{PBE0}} = \alpha E_{\text{X}}^{\text{HF}} + (1 - \alpha) E_{\text{X}}^{\text{PBE}} + E_{\text{C}}^{\text{PBE}}$$

Hartree-Fock exchange – the problem

$$E_X^{\text{HF}} = -\frac{1}{2} \sum_{i,j,k,l} D_{il} D_{jk} \underbrace{\int \frac{\varphi_i(\mathbf{r})\varphi_k(\mathbf{r})\varphi_j(\mathbf{r}')\varphi_l(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r'}_{\text{electron repulsion integrals}}$$



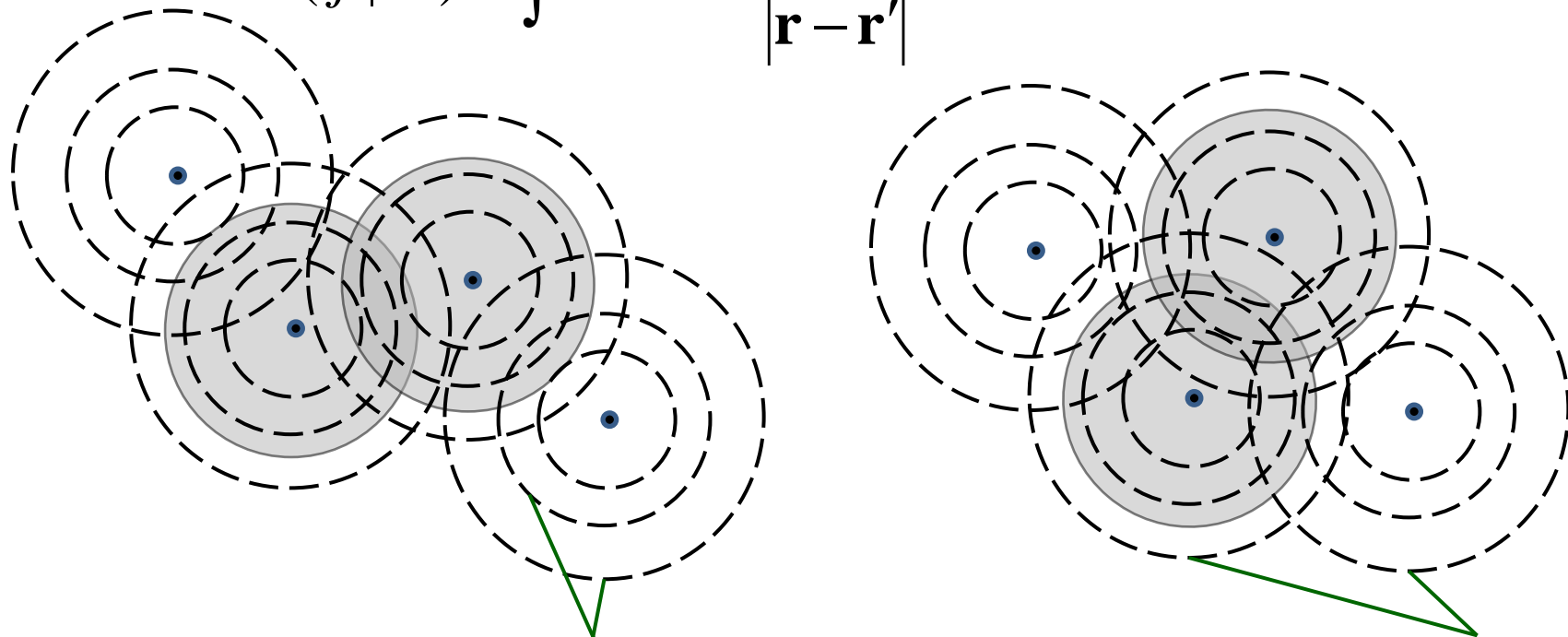
Lots of integrals, naïve implementation $\rightarrow N^4$ scaling (storage impractical for $N > 500$ basis functions)



- need fast evaluation
- need efficient use of sparsity (screening)

“Resolution of identity” (RI) (density fitting)

$$(ij | kl) = \int \frac{\varphi_i(\mathbf{r})\varphi_j(\mathbf{r})\varphi_k(\mathbf{r}')\varphi_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r'$$



$$\varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) = \sum_{\mu} C_{ij}^{\mu} P_{\mu}(\mathbf{r})$$

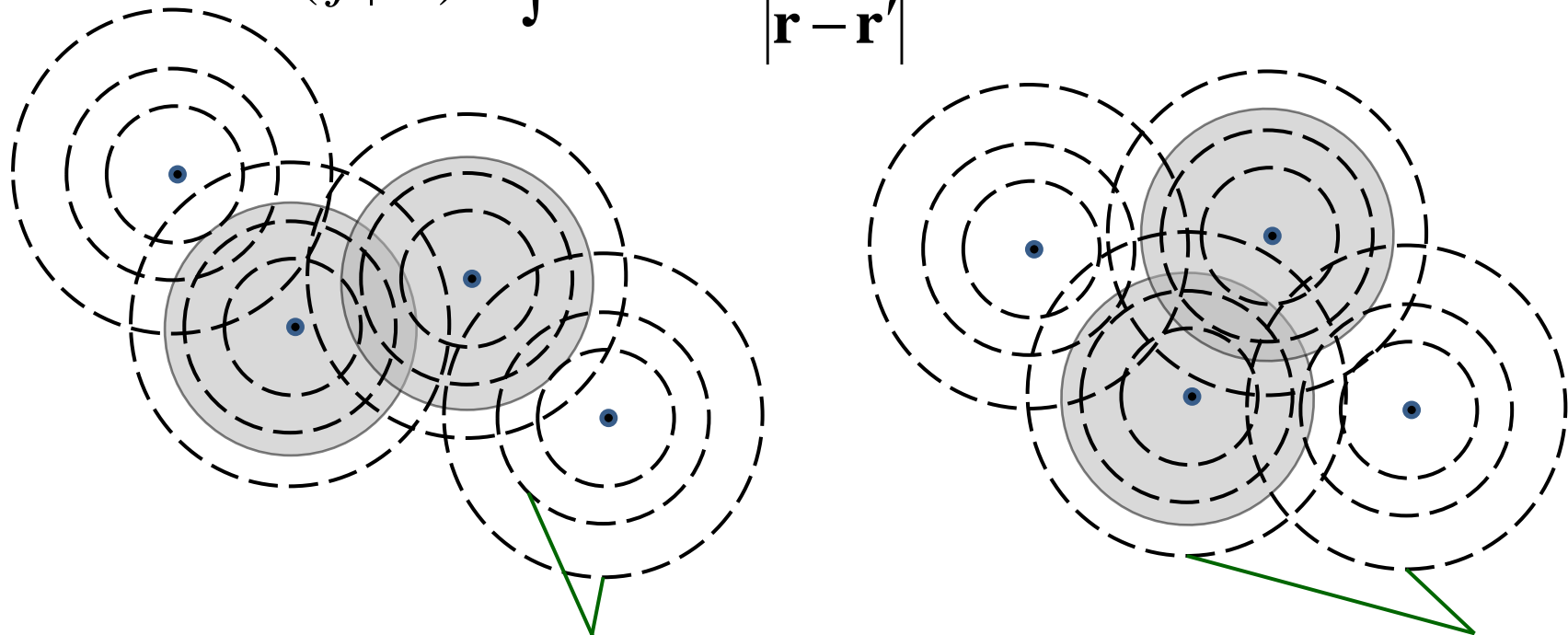
$$\varphi_k(\mathbf{r})\varphi_l(\mathbf{r}) = \sum_{\mu} C_{kl}^{\mu} P_{\mu}(\mathbf{r})$$

independent auxiliary basis

Basis-pair space is overcomplete, since $\{\varphi_i(\mathbf{r})\}$ approaches completeness \rightarrow size of $\{P_{\mu}(\mathbf{r})\} \sim 4\text{-}5$ times size of $\{\varphi_i(\mathbf{r})\}$

“Resolution of identity” (RI) (density fitting)

$$(ij | kl) = \int \frac{\varphi_i(\mathbf{r})\varphi_j(\mathbf{r})\varphi_k(\mathbf{r}')\varphi_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r'$$



$$\varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) = \sum_{\mu} C_{ij}^{\mu} P_{\mu}(\mathbf{r})$$

$$\varphi_k(\mathbf{r})\varphi_l(\mathbf{r}) = \sum_{\mu} C_{kl}^{\mu} P_{\mu}(\mathbf{r})$$

independent auxiliary basis

Finding the RI coefficients: RI-SVS

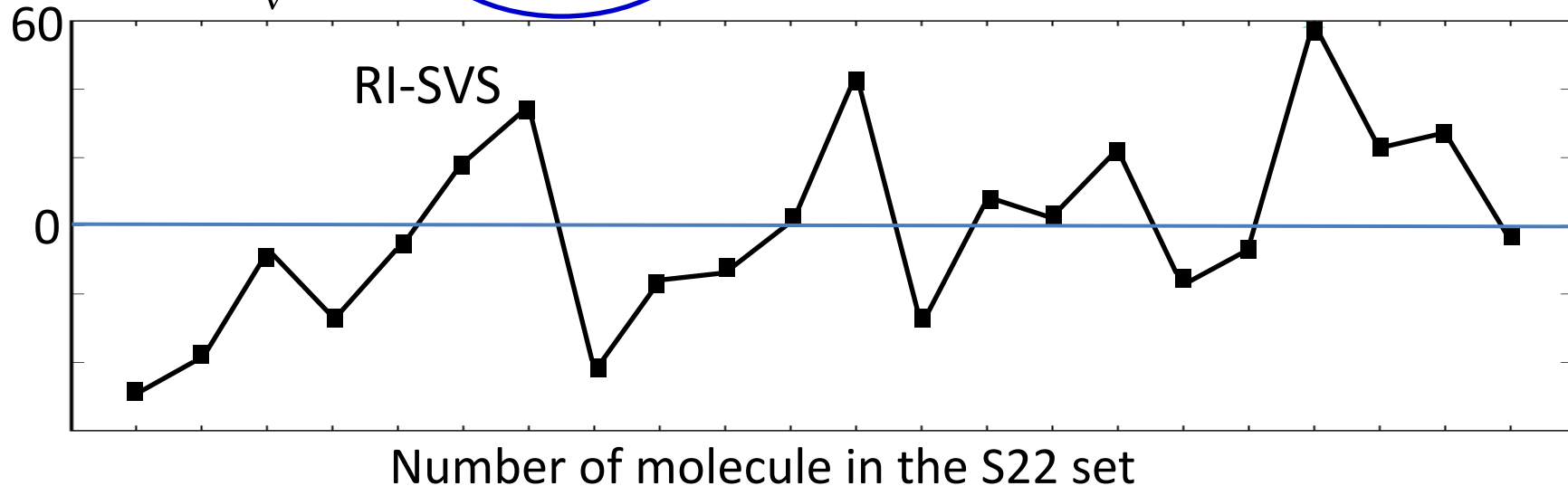
$$\varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) \approx \sum_{\mu} C_{ij}^{\mu} P_{\mu}(\mathbf{r}) \Rightarrow (ij | kl) \approx I_{ij,kl} = \sum_{\mu,\nu} C_{ij}^{\mu} V_{\mu\nu} C_{kl}^{\nu}$$

Minimize the error norm: $\min_C \int \left(\sum_{\mu} C_{ij}^{\mu} P_{\mu}(\mathbf{r}) - \varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) \right)^2 d^3 r$



$$I_{ij,kl} = \sum_{\nu} O_{ij}^{\nu} S_{\nu\sigma}^{-1} V_{\sigma\sigma'} S_{\sigma'\mu}^{-1} O_{kl}^{\mu}, \quad O_{ij}^{\nu} = \int \varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) P_{\nu}(\mathbf{r}) d^3 r$$

Error in total energy (meV)



Finding better RI coefficients

$$\rho_{ij}(\mathbf{r}) = \varphi_i(\mathbf{r})\varphi_j(\mathbf{r}), \quad (ij | kl) = \int \frac{\rho_{ij}(\mathbf{r})\rho_{kl}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r$$

Let us calculate the error in $(ij | ij)$ – the largest integrals:

$$\delta(ij | ij) = 2 \underbrace{\int \frac{\delta\rho_{ij}(\mathbf{r}) \left(\sum_v C_{ij}^v P_v(\mathbf{r}') \right)}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r'}_{\text{first-order correction does not vanish in RI-SVS!}} + \Delta(\delta\rho_{ij}^2)$$

first-order correction does not vanish in RI-SVS!

Is it possible to do better without increasing the size of the auxiliary basis?

Finding better RI coefficients: RI-V

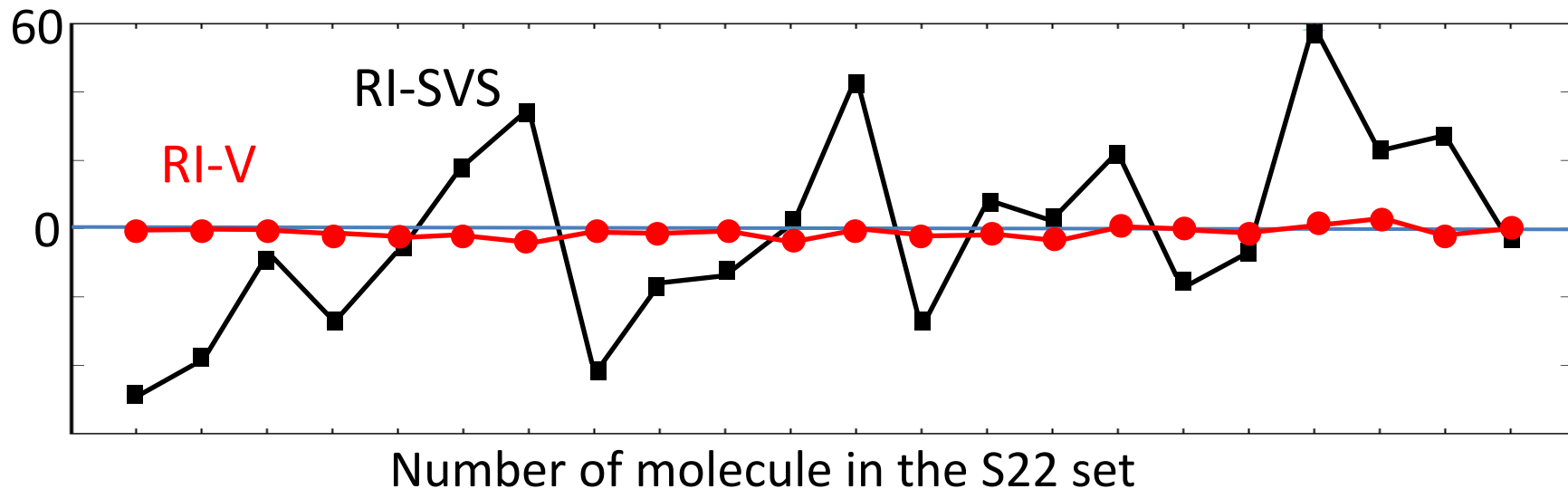
Set the first-order correction to zero, minimize second-order:

$$\Delta(\delta\rho_{ij}^2) \rightarrow \min \quad \Rightarrow \quad \Delta(\delta\rho_{ij}) \rightarrow 0$$

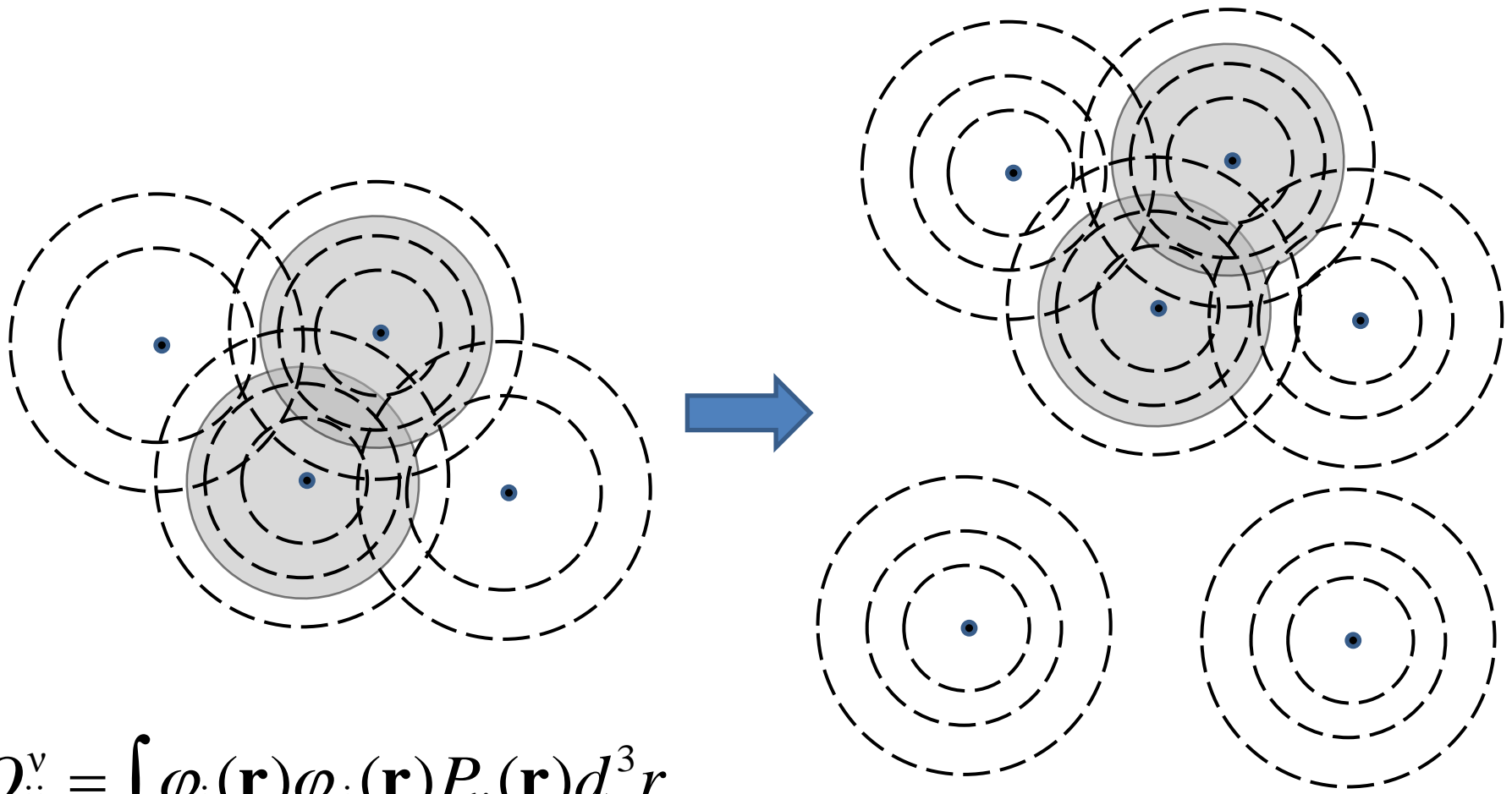


$$I_{ij,kl} = \sum_{\nu} Q_{ij}^{\nu} V_{\nu\mu}^{-1} Q_{kl}^{\mu}, \quad Q_{ij}^{\nu} = \int \frac{\varphi_i(\mathbf{r})\varphi_j(\mathbf{r})P_{\nu}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r'$$

Error in total energy (meV)



Finding better RI coefficients: RI-V

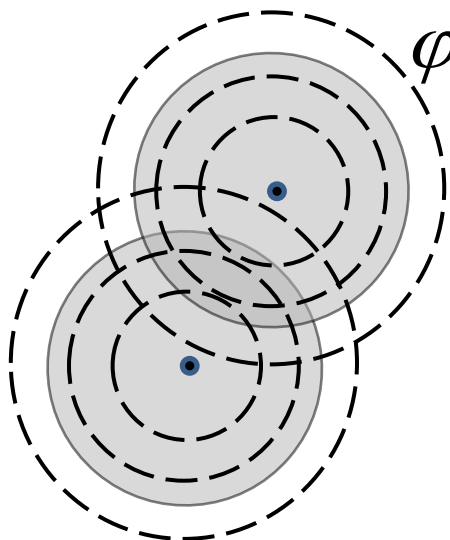


$$O_{ij}^v = \int \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}) P_v(\mathbf{r}) d^3 r$$

$$Q_{ij}^v = \int \frac{\varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}) P_v(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r'$$

Distant aux. functions contribute to the integrals → a lot of memory and operations → scaling N^3

Localized RI-V (RI-LVL, Jürgen Wieferink)



$$\varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) \approx \sum_{\mu} C_{ij}^{\mu} P_{\mu}(\mathbf{r}), \quad \mu \in \text{atom}(i) \text{ or } \text{atom}(j)$$

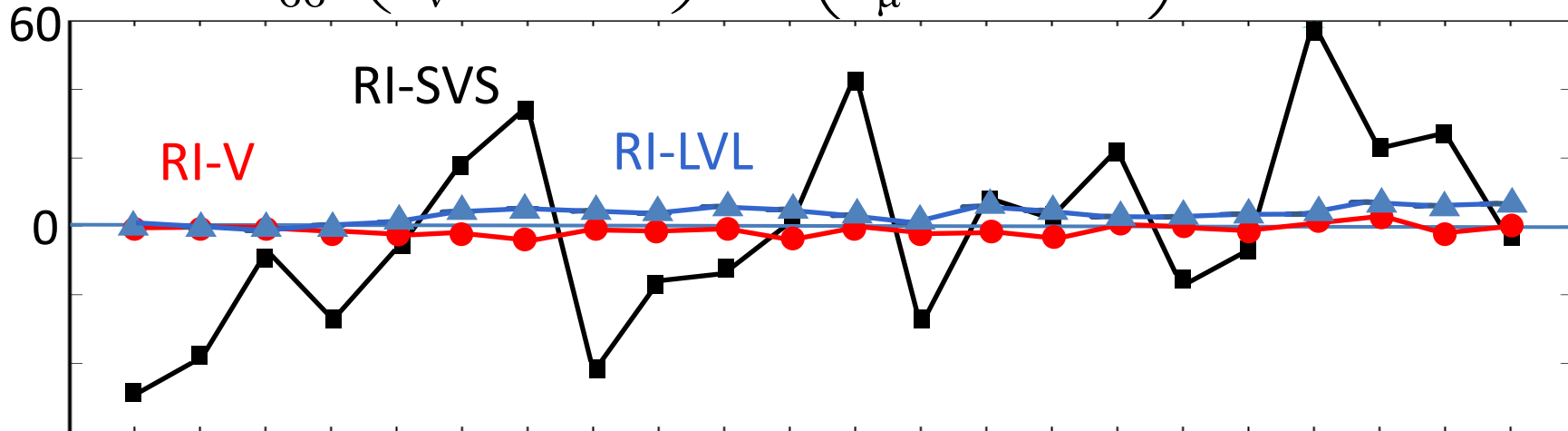
$$\Delta(\delta\rho_{ij}^2) \rightarrow \min \quad \Rightarrow \quad \Delta(\delta\rho_{ij}) \rightarrow 0$$



local inverse Coulomb matrix

$$I_{ij,kl} = \sum_{\sigma\sigma'} \left(\sum_{\nu} Q_{ij}^{\nu} L_{\nu\sigma} \right) V_{\sigma\sigma'} \left(\sum_{\mu} L_{\sigma'\mu} Q_{kl}^{\mu} \right), \quad L_{\nu\sigma} = (V^{-1})_{\nu\sigma}$$

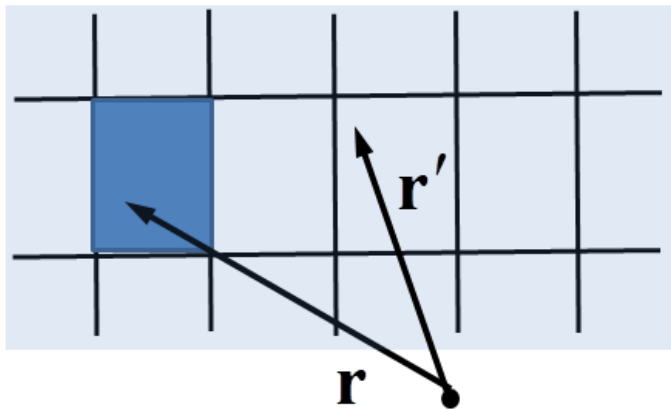
Error in total energy (meV)



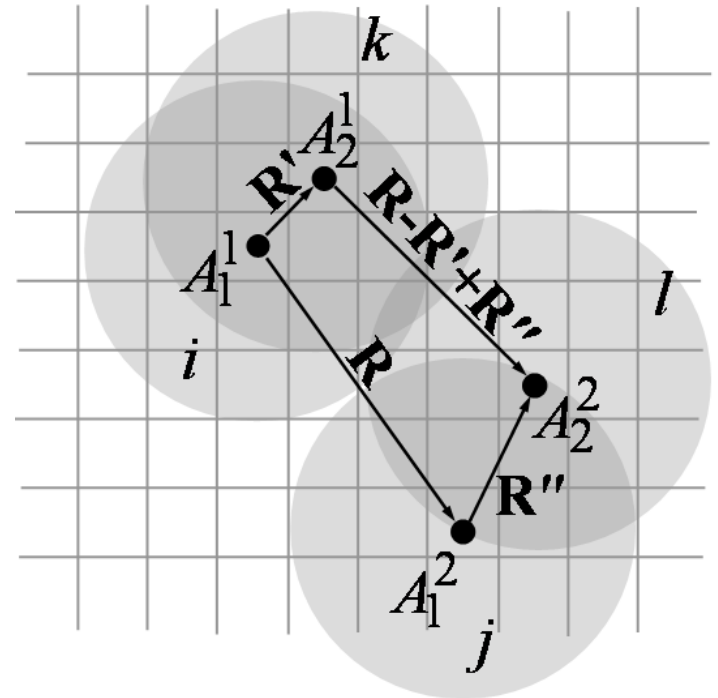
Number of molecule in the S22 set

Hartree-Fock exchange in extended systems

$$E_X^{\text{HF}} = -\frac{1}{2} \sum_{\substack{m,n \\ \mathbf{k}, \mathbf{k}'}} \int \frac{\psi_{m\mathbf{k}}^*(\mathbf{r}, \sigma) \psi_{n\mathbf{k}'}(\mathbf{r}, \sigma) \psi_{n\mathbf{k}'}^*(\mathbf{r}', \sigma') \psi_{m\mathbf{k}}(\mathbf{r}', \sigma')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r' d\sigma d\sigma'$$



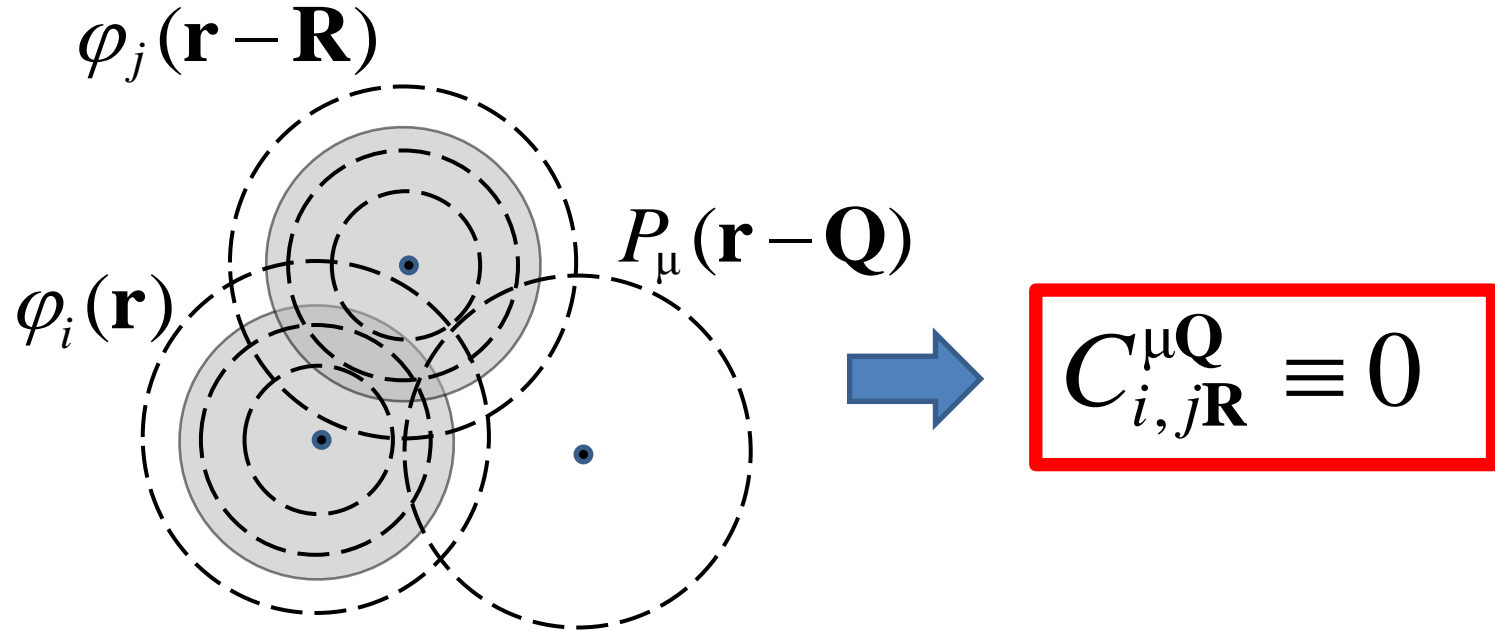
$$\psi_{m\mathbf{k}}(\mathbf{r}, \sigma) = s(\sigma) \sum_{i, \mathbf{R}} c_{mi}^{\mathbf{k}\sigma} \varphi_i(\mathbf{r} - \mathbf{R}) e^{i\mathbf{k}\mathbf{R}}$$



$$E_X^{\text{HF}} = -\frac{1}{2} \sum_{\substack{i,j,k,l \\ \mathbf{R}, \mathbf{R}', \mathbf{R}''}} D_{il}(\mathbf{R} + \mathbf{R}'') D_{jk}(\mathbf{R}' - \mathbf{R}) \times \\ \times \int \frac{\varphi_i(\mathbf{r}) \varphi_k(\mathbf{r} - \mathbf{R}') \varphi_j(\mathbf{r}' - \mathbf{R}) \varphi_l(\mathbf{r}' - \mathbf{R} - \mathbf{R}'')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r'$$

Electron repulsion integrals in periodic systems

RI-V is impractical for extended systems

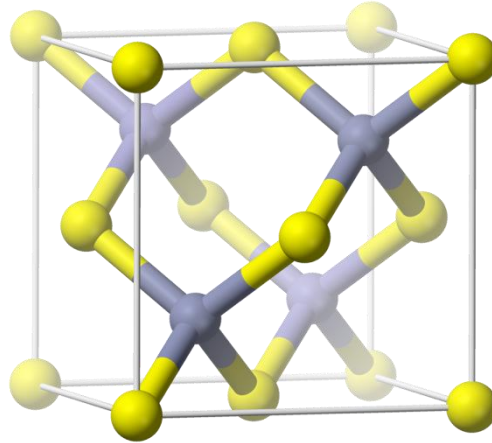


RI-LVL: Sparse, easier to calculate, linear scaling is possible!

$$I_{ij\mathbf{R}',k\mathbf{R}|\mathbf{R}+\mathbf{R}''} = \sum_{\mu\mathbf{Q}'} \sum_{\nu\mathbf{Q}''} C_{i,j\mathbf{R}'}^{\mu\mathbf{Q}'} V_{\mu\nu(\mathbf{R}+\mathbf{Q}''-\mathbf{Q}')} C_{k,l\mathbf{R}''}^{\nu\mathbf{Q}''}$$

Scaling

Zincblend GaAs, standard *tight* settings, PBE0 (no symmetry!)



System size (number of atoms / unit cell), 48 CPUs

<i>N</i> atoms, kpt	Time/iter (s)	Scaling expon.
2, 8x8x8	140	1
16, 4x4x4	900	0.9
128, 2x2x2	9500	1.1-1.0

$\sim O(N_{\text{atoms}})$ scaling!

Beyond mean-field for extended systems

What is the best way to validate a computational method?

What is the best way to validate a computational method?

Experiment

What is the best way to validate a computational method?

Experiment

Best possible theory

What is the best way to validate a computational method?

Experiment

Best possible theory

Exact solution within given well-defined approximations

Diffusion Monte Carlo (DMC) method

$$-\frac{\partial \Psi}{\partial(it)} = \hat{H}\Psi \Rightarrow \left(\frac{\partial}{\partial\tau} - \frac{1}{2} \sum_i \nabla^2 \right) \Psi = -V\Psi$$

Diffusion Monte Carlo (DMC) method

$$-\frac{\partial \Psi}{\partial(it)} = \hat{H}\Psi \Rightarrow \left(\frac{\partial}{\partial\tau} - \frac{1}{2} \sum_i \nabla^2 \right) \Psi = -V\Psi$$

Formal solution:

Green's function - solution of the same equation with initial condition $G(\{\mathbf{r}\}, \{\mathbf{r}'\}, 0) = \delta(\{\mathbf{r}\} - \{\mathbf{r}'\})$

$$\Psi(\{\mathbf{r}\}, \tau) = \int G(\{\mathbf{r}\}, \{\mathbf{r}'\}, \tau) \Psi(\{\mathbf{r}'\}, 0) d\{\mathbf{r}'\}$$

Diffusion Monte Carlo (DMC) method

$$-\frac{\partial \Psi}{\partial(it)} = \hat{H}\Psi \Rightarrow \left(\frac{\partial}{\partial\tau} - \frac{1}{2} \sum_i \nabla^2 \right) \Psi = -V\Psi$$

Formal solution:

Green's function - solution of the same equation with initial condition $G(\{\mathbf{r}\}, \{\mathbf{r}'\}, 0) = \delta(\{\mathbf{r}\} - \{\mathbf{r}'\})$

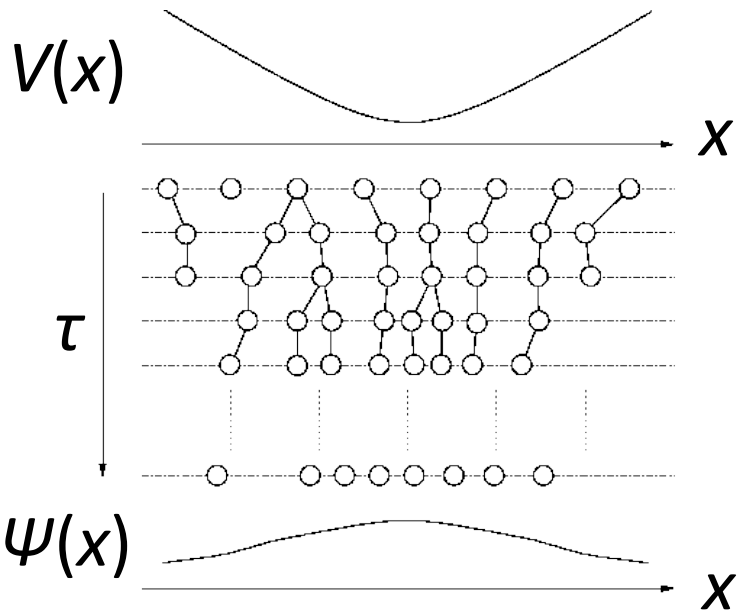
$$\Psi(\{\mathbf{r}\}, \tau) = \int G(\{\mathbf{r}\}, \{\mathbf{r}'\}, \tau) \Psi(\{\mathbf{r}'\}, 0) d\{\mathbf{r}'\}$$

$$\hat{H}\Psi_i = E_i\Psi_i \Rightarrow G(\{\mathbf{r}\}, \{\mathbf{r}'\}, \tau) = \sum_i \Psi_i(\{\mathbf{r}\}) e^{-\tau E_i} \Psi_i^*(\{\mathbf{r}'\})$$

only ground state survives

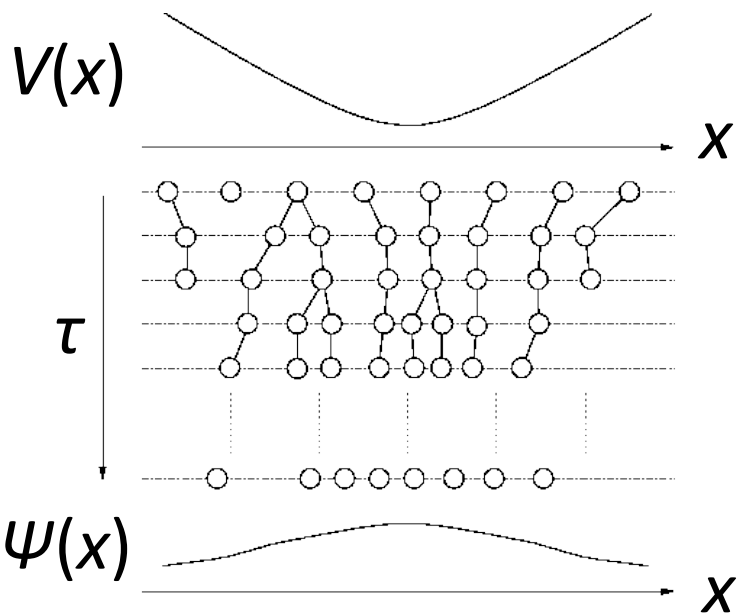
$$\lim_{\tau \rightarrow \infty} \Psi(\{\mathbf{r}\}, \tau) = \lim_{\tau \rightarrow \infty} \Psi_0(\{\mathbf{r}\}) e^{-\tau(E_0 - E_T)} \langle \Psi_0 | \Phi_{\text{init}} \rangle$$

DMC advantages and disadvantages



Brownian particles
 \Updownarrow
distribution function $\psi(x)$

DMC advantages and disadvantages

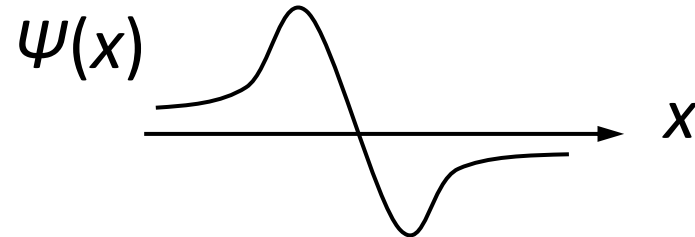


Brownian particles



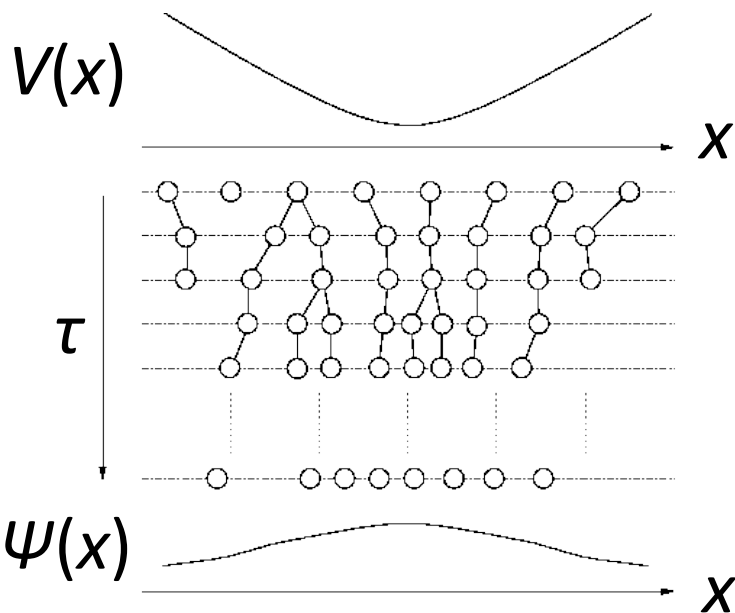
distribution function $\psi(x)$

Electronic wave functions



distribution changes sign! (sign problem)

DMC advantages and disadvantages

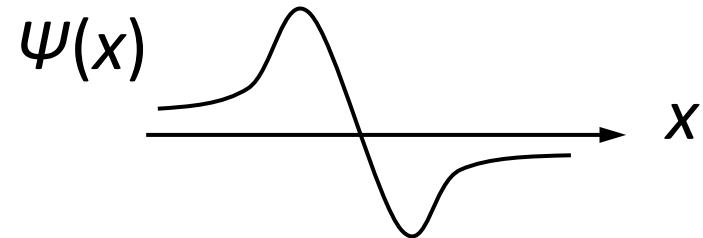


Brownian particles



distribution function $\psi(x)$

Electronic wave functions

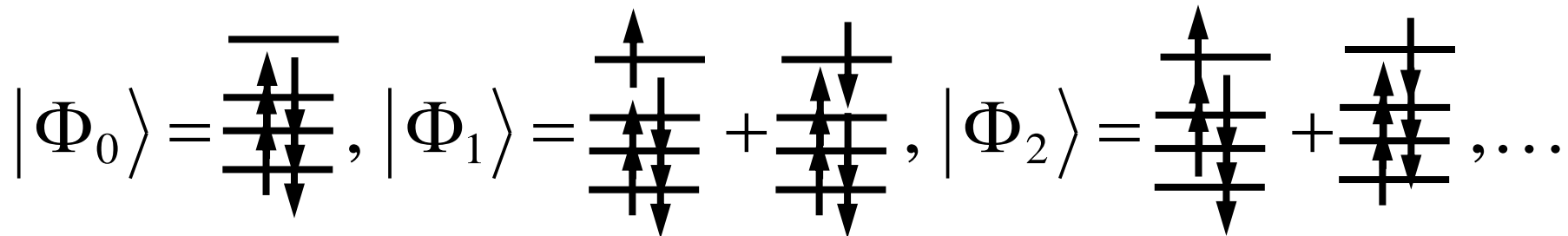


distribution changes sign! (sign problem)

- + **Very accurate for small systems**
- + **linear scaling implementations were demonstrated , easily parallelizable on many CPUs**
- **Sign problem (especially solids) \rightarrow fixed-node approximation (solutions exist, but computationally expensive)**
- **Computational cost increases as Z^6 in all-electron calculations \rightarrow need pseudopotentials**
- **Accurate calculation of energy gradients is difficult**

The concept of mixing excitations

$\hat{H}_0 \Phi_i = E_i^0 \Phi_i$ – non-interacting effective particles (HF, DFT, etc.)



$\{\Phi_i\}$ – a basis set for N -electron wave functions



$$\Psi_i = \sum_j c_{ij} \Phi_j, [\hat{H}_0 + (\hat{H} - \hat{H}_0)] \sum_j c_{ij} \Phi_j = E_i \sum_j c_{ij} \Phi_j$$

Project onto $\langle \Phi_k | \rightarrow$ equations for c_{ij} :

$$\sum_j c_{ij} \langle \Phi_k | \Delta \hat{H} | \Phi_j \rangle = (E_i - E_k^0) c_{ik}$$

configuration interaction

Configuration interaction – matrix diagonalization

	Φ_0	Φ_i^a	Φ_{ij}^{ab}	$\frac{M!}{(M-n)!n!}$	n -tuple excitations
Φ_0	$\langle \Phi_0 \hat{H} \Phi_0 \rangle$	$\langle \Phi_0 \hat{H} \Phi_i^a \rangle$		
Φ_i^a	$\langle \Phi_i^a \hat{H} \Phi_0 \rangle$	$\langle \Phi_j^b \hat{H} \Phi_i^a \rangle$		
Φ_{ij}^{ab}		

$$\Psi = \Phi_0 + \sum_{i,a} c_i^a \Phi_i^a + \sum_{ij,ab} c_{ij}^{ab} \Phi_{ij}^{ab} + \dots$$

Full configuration interaction (FCI)

$$\Psi_i = \sum_j c_{ij} \Phi_j \quad \text{– include ALL excitations of } N \text{ electrons on } M \text{ orbitals (} M \text{ is determined by the basis set size)}$$

+ FCI is exact within given basis set

+ The result does not depend on the choice of orbitals in Φ_0

+ Gives ground and excited states

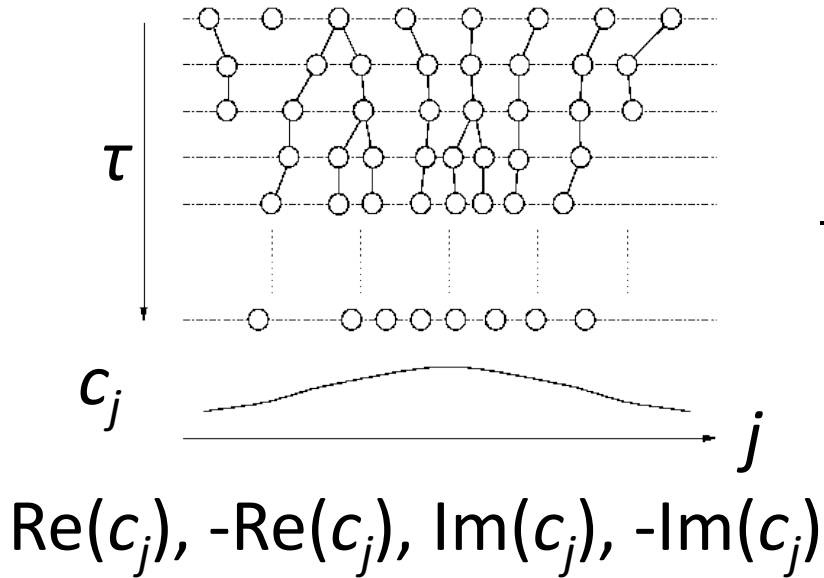
- The scaling with system size is combinatorial: $\frac{M!}{(M-N)!N!}$

50 electrons on 100 orbitals $\rightarrow 10^{29} \times 10^{29}$ matrix diagonalization

Sparsity: $\langle \Phi^{(n)} | \hat{H} | \Phi^{(n\pm 2)} \rangle \neq 0$; need to evaluate ERIs

FCI quantum Monte Carlo (FCIQMC) method

Walkers – determinants



$$\Psi_0 = \sum_j c_j \Phi_j$$

$$-\frac{dN_i}{d\tau} = (\langle \Phi_i | \hat{H} | \Phi_i \rangle - E_T) N_i + \sum_{j \neq i} \langle \Phi_i | \hat{H} | \Phi_j \rangle N_j$$

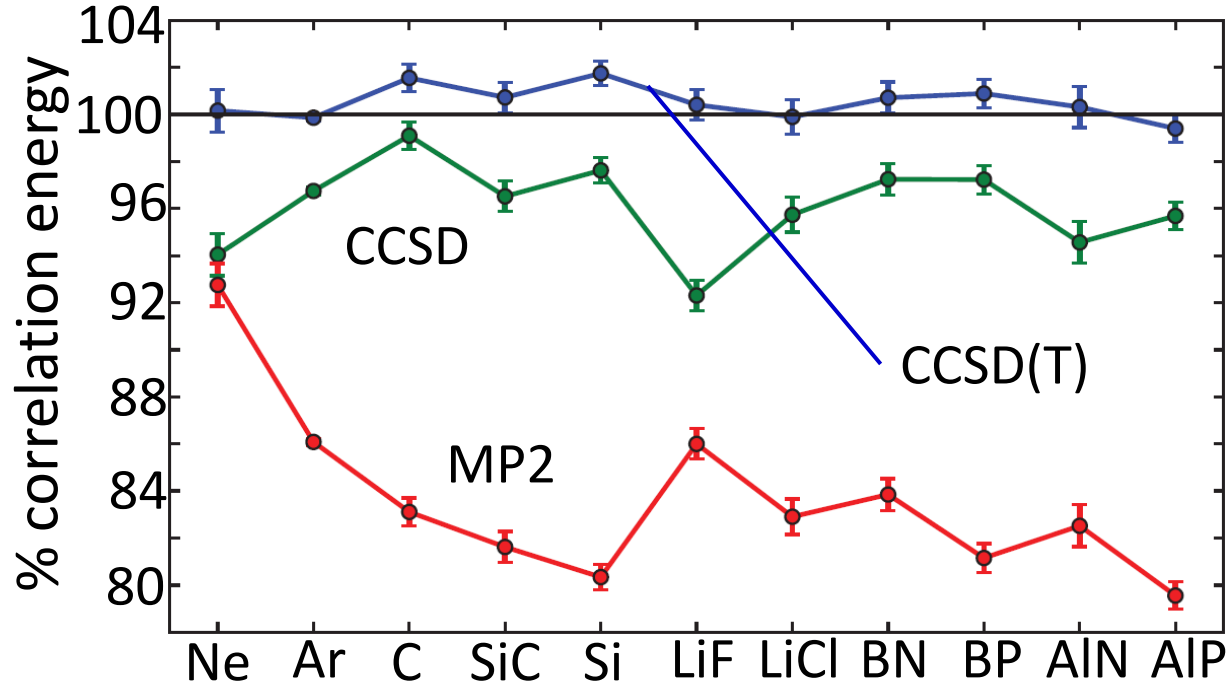


$$E, \quad c_i = (-1)^{x_i} \sqrt{\frac{\langle N_i \rangle}{\langle N \rangle}}$$

No sign problem (positive and negative coefficients can be evolved independently)

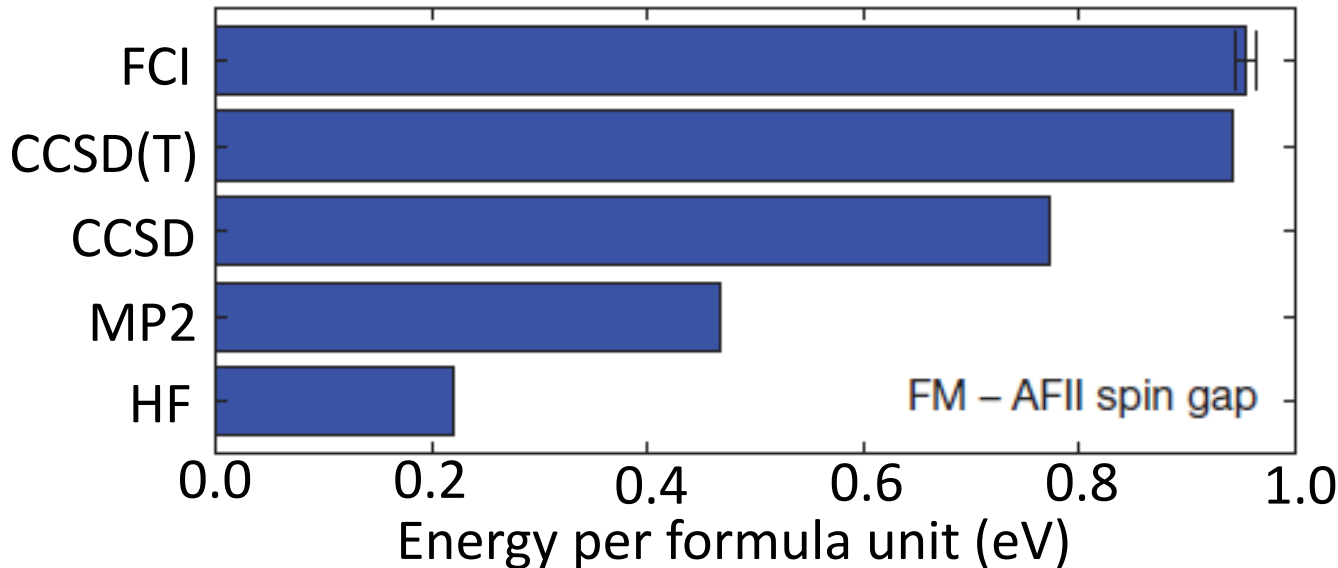
Timing example: diamond, 4x4x4 k-points – 25,000 CPU hours, ± 20 meV per atom remaining error in correlation energy

FCI quantum Monte Carlo (FCIQMC) method



Percent of correlation energy captured by different methods relative to FCI (VASP, PAW)

Ferromagnetic-antiferromagnetic spin gap in NiO (VASP, PAW)



FM - AFII spin gap

Booth, Grüneis, Kresse, and Alavi, Nature **493**, 365 (2013)

Hierarchies of GS wave-function methods

Truncated CI
(CISD, CISDT,...)

$$|\Psi_0^{\{m\}}\rangle = \sum_{i \leq m} \hat{T}_i |\Phi_0\rangle$$

CI{m}: $\sim n^m N^{m+2}$

Møller-Plesset
perturbation theory
(MP2, MP3, MP4,...)

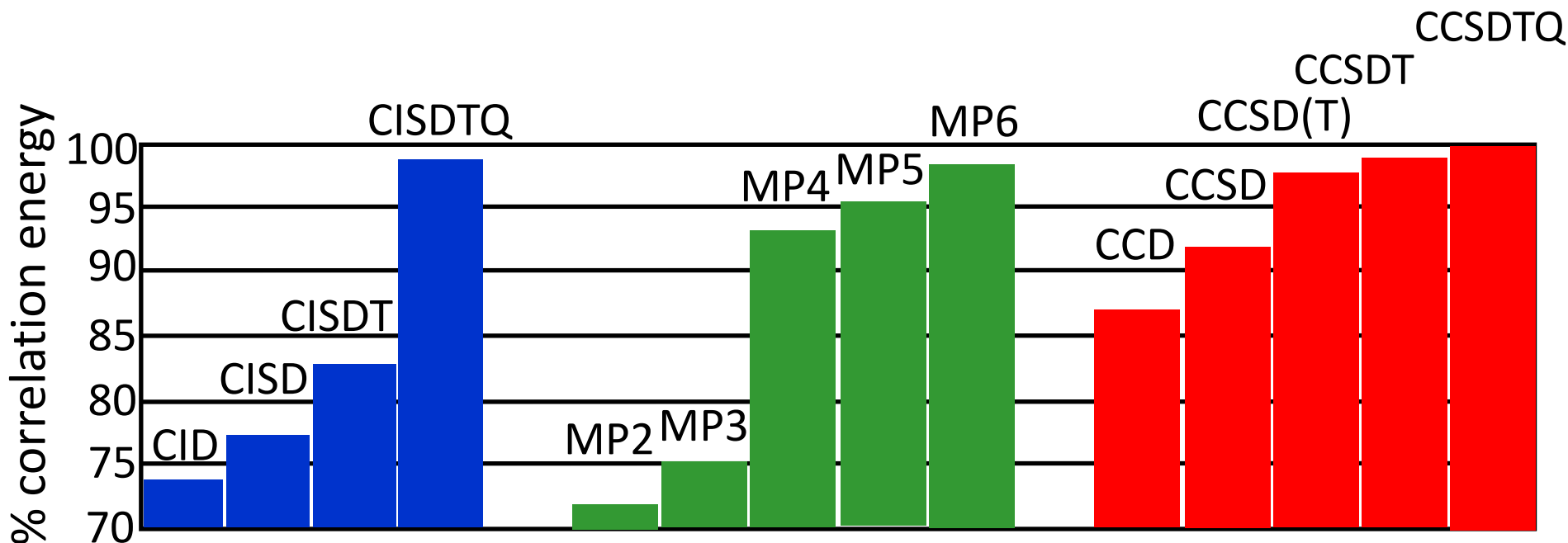
$$E_0^{(2)} = \sum_{i \neq 0} \frac{|\langle \Phi_0 | \hat{H}' | \Phi_i \rangle|^2}{E_0^{(0)} - E_i^{(0)}}$$

MPm: $\sim n N^{m+2}$

Coupled-cluster
(CCD, CCSD, CCSDT,...)

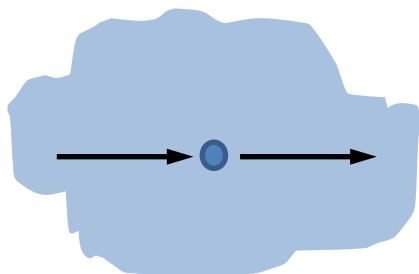
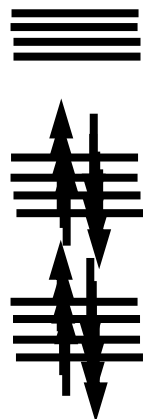
$$|\Psi_0^{\{m\}}\rangle = e^{\sum_{i \leq m} \hat{T}_i} |\Phi_0\rangle$$

CC{m}: $\sim n^m N^{m+2}$

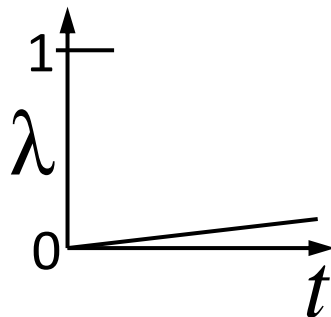


Ripples in the charged Fermi liquid

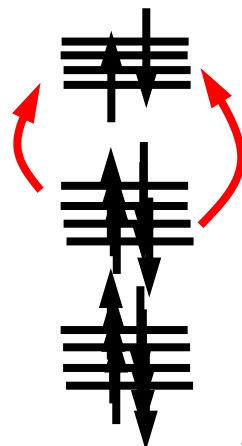
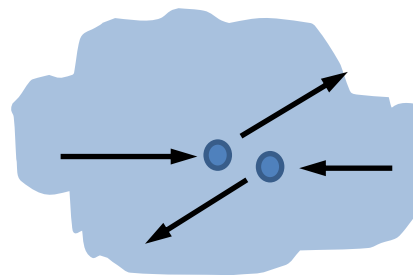
$$\hat{H}_0 \Phi_0 = E_0 \Phi_0$$



$$\hat{H}_0 \rightarrow \hat{H}_0 + \lambda V$$

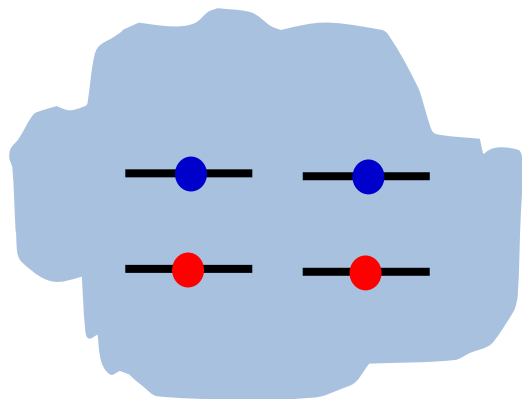


adiabatic switching

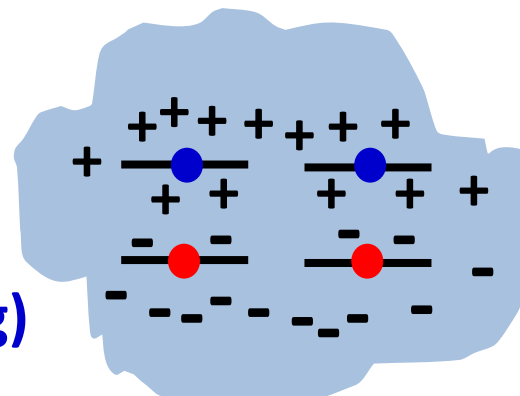


$$E_0^{(2)} = \sum_i \frac{|\langle \Phi_0 | \lambda V | \Phi_i \rangle|^2}{E_0^{(0)} - E_i^{(0)}}$$

fluctuating charge density



polarization (screening)



Long-range correlation (screening) contributions can be summed up to infinite order (EX+cRPA, rPT2, GW, BSE)

Random-phase approximation

Second-order energy correction (MP2, HF orbitals):

$$E_0^{(2)} = \sum_i \frac{|\langle \Phi_0 | V | \Phi_i \rangle|^2}{E_0^{(0)} - E_i^{(0)}} = \sum_{ij,ab} \frac{2(ia | jb)((ia | jb) - (ib | ja))}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

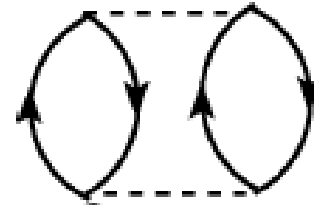
$$(ia | jb) = \int \frac{\psi_i^*(\mathbf{r})\psi_a(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_b(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Random-phase approximation

Second-order energy correction (MP2, HF orbitals):

$$E_0^{(2)} = \sum_i \frac{|\langle \Phi_0 | V | \Phi_i \rangle|^2}{E_0^{(0)} - E_i^{(0)}} = \sum_{ij,ab} \frac{2(ia | jb)((ia | jb) - (ib | ja))}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

$$(ia | jb) = \int \frac{\psi_i^*(\mathbf{r})\psi_a(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_b(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$



correlation



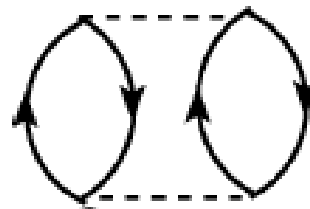
exchange

Random-phase approximation

Second-order energy correction (MP2, HF orbitals):

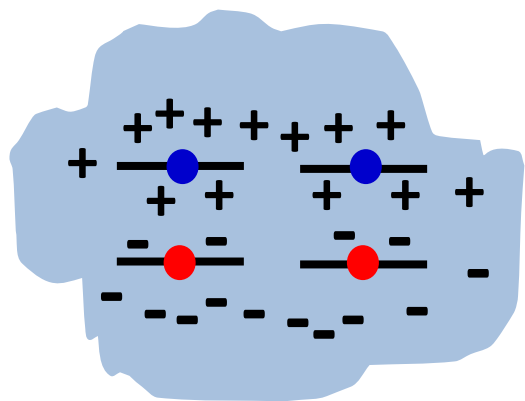
$$E_0^{(2)} = \sum_i \frac{|\langle \Phi_0 | V | \Phi_i \rangle|^2}{E_0^{(0)} - E_i^{(0)}} = \sum_{ij,ab} \frac{2(ia | jb) \left((ia | jb) - (ib | ja) \right)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

$$(ia | jb) = \int \frac{\psi_i^*(\mathbf{r}) \psi_a(\mathbf{r}) \psi_j^*(\mathbf{r}') \psi_b(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$



correlation

exchange



$$E_c = \text{[correlation diagram]} + \text{[exchange diagram]} + \dots$$

$$\sum_{ia,jb,kc} \frac{(ia | jb)(jb | kc)(kc | ia)}{(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)(\epsilon_i + \epsilon_k - \epsilon_a - \epsilon_c)}$$

Random-phase approximation and beyond

$$E_c^{\text{RPA}} = \text{[diagrams: two bubbles, two bubbles with a dashed line, and a bubble with a loop]} + \dots$$

$$E_c^{\text{RPA}} = \int_0^\infty \left[\ln(\det(1 - \{\chi_0(\omega)V\}_{\mu\nu})) + \text{Tr}(\{\chi_0(\omega)V\}_{\mu\nu}) \right] d\omega$$

Kohn-Sham polarizability:

$$\chi_0(\mathbf{r}, \mathbf{r}', \omega) = \sum_i^{\text{occ}} \sum_a^{\text{unocc}} \frac{\psi_i^*(\mathbf{r})\psi_a(\mathbf{r})\psi_a^*(\mathbf{r}')\psi_i(\mathbf{r}')}{i\omega - (\epsilon_a - \epsilon_i)} + \text{c.c.}$$

Renormalized second-order perturbation theory (rPT2):

$$E_c^{\text{rPT2}} = \text{[diagrams: single excitation with blue dashed lines, two bubbles, two bubbles with a loop, two crossed bubbles, and two crossed bubbles with a loop]} + \dots$$

single excitations

RPA

second-order screened exchange

Conclusions

- **Practically all beyond-DFT methods involve calculation of the electron repulsion integrals (ERIs)**
- **ERIs can be evaluated efficiently by using resolution of identity (density fitting) and taking into account sparsity**
- **Wave function methods slowly but steadily enter the arena of condensed matter physics**
- **Exploration of the connection between wave-function methods (coupled-cluster) and many-body perturbation theory (beyond RPA) continues**

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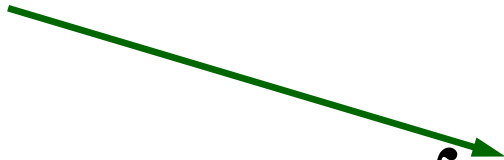
Matthias Scheffler



Finding better RI coefficients: RI-V

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \int V^{\frac{1}{2}}(\mathbf{r}, \mathbf{r}'') V^{\frac{1}{2}}(\mathbf{r}', \mathbf{r}'') d^3 r''$$

$$\int \underbrace{\varphi_i(\mathbf{r}'') \varphi_j(\mathbf{r}'') V^{\frac{1}{2}}(\mathbf{r}, \mathbf{r}'') d^3 r''}_{\text{green bracket}} \approx \sum_{\nu} C_{ij}^{\nu} \int P_{\nu}(\mathbf{r}'') V^{\frac{1}{2}}(\mathbf{r}, \mathbf{r}'') d^3 r''$$


$$(ij | ij) = \int \tilde{\rho}_{ij}(\mathbf{r})^2 d^3 r$$

$$(ij | ij) = \int \tilde{\rho}_{ij}(\mathbf{r})^2 d^3 r, \quad \tilde{\rho}_{ij}(\mathbf{r}) = \int \varphi_i(\mathbf{r}'') \varphi_j(\mathbf{r}'') V^{\frac{1}{2}}(\mathbf{r}, \mathbf{r}'') d^3 r''$$