Review of the major families of electronic-structure computational methods in quantum chemistry

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The quantum many-body electronic-structure problem

- N**-electron Hamiltonian** in the Born-Oppenheimer and non-relativistic approximations:

$$H(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = -\frac{1}{2}\sum_{i=1}^{N} \Delta_{\mathbf{r}_i} + \sum_{i=1}^{N} v_{\text{ne}}(\mathbf{r}_i) + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\ j\neq i}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- Stationary states are determined by the **time-independent Schrödinger equation**:

$$H(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = E\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$$

  where $\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$ is a **wave function** written with space-spin coordinates $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$ (with $\mathbf{r}_i \in \mathbb{R}^3$ and $\sigma_i =\uparrow$ or $\downarrow$), and E is the associated energy.

- Because electrons are fermions, the wave function must be **antisymmetric** with respect to the exchange of two coordinates:

$$\Psi(..., \mathbf{x}_i, ..., \mathbf{x}_j, ...) = -\Psi(..., \mathbf{x}_j, ..., \mathbf{x}_i, ...)$$

- Using **Dirac notations**, the Schrödinger equation can be rewritten in a convenient representation-independent formalism:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \quad \text{with} \quad \hat{H} = \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}$$

- We want an **approximation to the wave function** Ψ **and the associated energy** E of a specific state, most often the ground-state wave function Ψ_0 and the ground-state energy E_0.

Outline

1. Wave-function theory (WFT)
2. Density-functional theory (DFT)
3. Quantum Monte Carlo (QMC)

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The Hartree-Fock (HF) starting point

- In HF, we approximate the wave function by a **single Slater determinant**:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) \approx \Phi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \psi_1(\mathbf{x}_1) \wedge \psi_2(\mathbf{x}_2) \wedge ... \wedge \psi_N(\mathbf{x}_N)$$

  with orthonormal **spin orbitals** $\psi_i(\mathbf{x}) = \phi_i(\mathbf{r})\chi_{\sigma_i}(\sigma)$ which are products of spatial orbitals $\phi_i(\mathbf{r})$ with a spin function $\chi_{\sigma_i}(\sigma) = \delta_{\sigma_i,\sigma}$.

- The spin orbitals are determined by **minimizing the HF energy** $E_{\text{HF}} = \langle\Phi|\hat{H}|\Phi\rangle$ (with orthonormalization constraints) leading to the **HF equations**:

$$\left(-\frac{1}{2}\Delta_{\mathbf{r}} + v_{\text{ne}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r})\right)\psi_i(\mathbf{x}) + \int v_{\text{x}}^{\text{HF}}(\mathbf{x},\mathbf{x}')\psi_i(\mathbf{x}')\text{d}\mathbf{x}' = \varepsilon_i\psi_i(\mathbf{x})$$

  with the Hartree potential $v_{\text{H}}(\mathbf{r})$ and the HF exchange potential $v_{\text{x}}^{\text{HF}}(\mathbf{x},\mathbf{x}')$

$$v_{\text{H}}(\mathbf{r}) = \sum_{j=1}^{N}\int\frac{\psi_j^*(\mathbf{x}')\psi_j(\mathbf{x}')}{|\mathbf{r}'-\mathbf{r}|}\text{d}\mathbf{x}' \quad \text{and} \quad v_{\text{x}}^{\text{HF}}(\mathbf{x},\mathbf{x}') = -\sum_{j=1}^{N}\frac{\psi_j^*(\mathbf{x}')\psi_j(\mathbf{x})}{|\mathbf{r}'-\mathbf{r}|}$$

- In practice, the orbitals are expanded on a **basis set**:

$$\phi_i(\mathbf{r}) = \sum_{\mu=1}^{M} c_{\mu i} f_\mu(\mathbf{r})$$

  where the basis functions $f_\mu(\mathbf{r})$ are usually polynomials × decreasing Gaussian function centered on nuclei ("Gaussian basis sets"). Computational cost $= \mathcal{O}\left(M^4\right)$

- **Occupied ($i \leq N$) and virtual ($i > N$) HF spin orbitals are used as a starting point for post-HF methods.**

A straightforward post-HF method: Full configuration interaction (FCI)

- In FCI, **the wave function is expanded in terms of the HF determinant Φ, the singly excited determinants Φ_i^a, the doubly excited determinants Φ_{ij}^{ab}, and so on**:

$$|\Psi_{\text{FCI}}\rangle = c_0|\Phi\rangle + \sum_{i}^{\text{occ}}\sum_{a}^{\text{vir}} c_i^a|\Phi_i^a\rangle + \sum_{i<j}^{\text{occ}}\sum_{a<b}^{\text{vir}} c_{ij}^{ab}|\Phi_{ij}^{ab}\rangle + \sum_{i<j<k}^{\text{occ}}\sum_{a<b<c}^{\text{vir}} c_{ijk}^{abc}|\Phi_{ijk}^{abc}\rangle + \cdots$$

  and the coefficients $c_0, c_i^a, c_{ij}^{ab}, \ldots$ are found by minimizing the FCI energy $E_{\text{FCI}} = \langle\Psi_{\text{FCI}}|\hat{H}|\Psi_{\text{FCI}}\rangle$ (with the normalization constraint of the wave function) corresponding to diagonalizing $\hat{H}$ in the space spanned by all determinants.

- In the limit of a **complete basis set** ($M \to \infty$), **FCI becomes exact**.

- Compared to HF, FCI brings **electron correlation**. The **correlation energy** is defined as

$$E_{\text{c}} = E_{\text{exact}} - E_{\text{HF}}$$

  and is the most important quantity targeted by post-HF methods. **The correlation energy has a slow convergence with the basis size**: error on $E_{\text{c}} = \mathcal{O}\left(M^{-1}\right)$

- **Combinatorial explosion of number of determinants**: $N_{\text{det}} \approx \binom{M}{N} = \mathcal{O}\left(M^N\right)$
  $\Longrightarrow$ necessity to find low-power-scaling approximations

- To develop approximations to FCI, we identify **two regimes of electron correlation**: **dynamic (or weak) correlation** and **static (or strong) correlation**

Post-HF methods for dynamic/weak correlation: single-reference methods

- **Correlation is called "dynamic" or "weak" if** $c_i^a, c_{ij}^{ab}, \ldots \ll c_0$
  $\Longrightarrow$ HF is a good starting point

- This corresponds to situations with a **large HOMO-LUMO HF gap**.
  Example: He atom, H_2 molecule at equilibrium distance.

- ⚠ Even if each coefficient is small, their total contribution can be large.

- For dynamic correlation, one considers **"single-reference" methods** which are approximations to FCI **assuming the predominance of the single HF determinant**.

- Three main families of single-reference post-HF methods:
  - **Truncated configuration interaction (CI)**
  - **Møller-Plesset (MP) perturbation theory (PT)**
  - **Coupled-cluster (CC) theory**

Single-reference truncated configuration interaction (CI)

- The FCI wave function is **truncated at a given excitation level**, e.g. keeping only single and double excitations (CISD):

$$|\Psi_{\text{CISD}}\rangle = |\Phi\rangle + \sum_{i}^{\text{occ}} \sum_{a}^{\text{vir}} c_i^a |\Phi_i^a\rangle + \sum_{i<j}^{\text{occ}} \sum_{a<b}^{\text{vir}} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle$$

  Remark: it was chosen $c_0 = 1$ (intermediate normalization)

- The coefficients c_i^a, c_{ij}^{ab} are found by **minimizing the CISD energy** $E_{\text{CISD}} = \langle \Psi_{\text{CISD}} | \hat{H} | \Psi_{\text{CISD}} \rangle \implies$ according to the **variational theorem**: $E_{\text{CISD}} \geq E_{\text{exact}}$.
- Computational cost $= \mathcal{O}\left(M^6\right)$
- **Serious shortcoming of truncated CI: it is not size-consistent**.
- We prefer methods that satisfy the **size-consistency property**: the total energy of a system composed of two non-interacting fragments A and B is equal to the sum of the total energies of the separate fragments:

$$E(A+B) = E(A) + E(B)$$

  This property is important in chemistry. There is also the related **size-extensity property**: $E(N) \propto N$ for $N \to \infty$ which is important for extended systems.

Single-reference Møller-Plesset (MP) perturbation theory

- **Perturbation theory starting from the HF Hamiltonian**: $\hat{H} = \hat{H}_{\text{HF}} + \left(\hat{W}_{\text{ee}} - \hat{V}_{\text{Hx}}^{\text{HF}}\right)$
- The first-order wave function (MP1) includes only doubly excited determinants:

$$|\Psi_{\text{MP1}}\rangle = \sum_{i<j}^{\text{occ}} \sum_{a<b}^{\text{vir}} c_{ij}^{ab,(1)} |\Phi_{ij}^{ab}\rangle \;\; \text{with} \;\; c_{ij}^{ab,(1)} = -\frac{\langle \Phi_{ij}^{ab} | \hat{W}_{\text{ee}} | \Phi \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}$$

  where ε_k are HF orbital energies.

- The second-order energy gives the **MP2 correlation energy**:

$$E_{\text{c}}^{\text{MP2}} = \langle \Phi | \hat{W}_{\text{ee}} | \Psi_{\text{MP1}} \rangle = -\sum_{i<j}^{\text{occ}} \sum_{a<b}^{\text{vir}} \frac{|\langle \Phi_{ij}^{ab} | \hat{W}_{\text{ee}} | \Phi \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}$$

- **MP2 is not variational** (E_{MP2} can be lower than E_{exact}) **but is size-consistent**.
- Computational cost $= \mathcal{O}\left(M^5\right)$
- **MP2 is a simple largely used post-HF method that often reasonably accounts for dynamic/weak correlation**.
- However, **accuracy is limited by missing higher-order terms**.
  Including higher-order terms (MP3, MP4, etc...) can be computationally costly and the series does not generally converge!

Single-reference coupled-cluster (CC) theory

- In CC, the wave function is taken as **an exponential of a truncated excitation expansion**, e.g. with single and double excitations (CCSD):

$$|\Psi_{\text{CCSD}}\rangle = e^{\hat{T}_1+\hat{T}_2}|\Phi\rangle$$

where $\hat{T}_1 = \sum_{i}^{\text{occ}} \sum_{a}^{\text{vir}} t_i^a \; \hat{c}_a^\dagger \hat{c}_i$ and $\hat{T}_2 = \sum_{i<j}^{\text{occ}} \sum_{a<b}^{\text{vir}} t_{ij}^{ab} \; \hat{c}_a^\dagger \hat{c}_b^\dagger \hat{c}_j \hat{c}_i$ are operators generating singly and doubly excited determinants when acting on the HF wave function $|\Phi\rangle$.

- **The CCSD wave function contains all excited determinants of the FCI wave function**, but the coefficients of triply, quadruply, etc.. excited determinants are (antisymmetrized) products of the coefficients of singly and doubly excited determinants.
- **The amplitudes t_i^a and t_{ij}^{ab} are found by projecting the Schrödinger equation** $\hat{H}|\Psi_{\text{CCSD}}\rangle = E|\Psi_{\text{CCSD}}\rangle$ onto $\langle\Phi_i^a|$ and $\langle\Phi_{ij}^{ab}|$.
- **CCSD is not variational** (E_{CCSD} can be lower than E_{exact}) **but is size-consistent**.
- Computational cost $= \mathcal{O}\left(M^6\right)$
- **CCSD is more accurate than MP2** because it contains higher-order terms.
- Possiblity to perturbatively add the triple-excitation operator $\hat{T}_3$ in the expansion $\Longrightarrow$ **CCSD(T) which is often considered as the gold-standard for dynamic/weak correlation** with computational cost $= \mathcal{O}\left(M^7\right)$.

Post-HF methods for static/strong correlation: multi-reference methods

- **Correlation is called "static" or "strong" if there are some coefficients in the FCI expansion that are not small compared to c_0** $\Longrightarrow$ HF is NOT a good starting point
- This corresponds to situations with a **small HOMO-LUMO HF gap**.
  Example: Be atom, H_2 molecule at dissociation, transition metals (Fe, Cu, etc...).
- **Single-reference methods give too much importance to the HF determinant and tend to fail for static/strong correlation** (e.g., MP2 diverges for zero HOMO-LUMO HF gap).
- Instead of HF, we use now the **multiconfiguration self-consistent field (MCSCF) method** which is a multideterminant extension of HF:

$$E_{\text{MCSCF}} = \min_{\{c_n,\psi_i\}} \langle \Psi_{\text{MCSCF}} | \hat{H} | \Psi_{\text{MCSCF}} \rangle \quad \text{with} \quad | \Psi_{\text{MCSCF}} \rangle = \sum_n c_n | \Phi_n \rangle$$

  Usually, we include all determinants $|\Phi_n\rangle$ that can be generated from a small orbital subspace, called **complete active space (CAS)** $\Longrightarrow$ accounts for static/strong correlation but combinatorial explosion with the size of the active space!

- Starting from MCSCF, remaining dynamic/weak correlation can be added with **multi-reference (MR) methods**:
  - **MRCI** (Ex: MRCISD): not size-consistent but used for very small systems
  - **MRPT** (Ex: CASPT2, NEVPT2): fairly used but requires large enough CAS
  - **MRCC**: several proposed methods but no consensual method yet

Other methods/developments for electron correlation

For static/strong correlation:

- Static/strong correlation effets can sometimes be approximately describe by allowing **symmetry breaking** (mostly spin symmetry) in the wave function.
  Example: restricted HF (RHF) $\longrightarrow$ unrestricted HF (UHF)
- A lot of attempts to build compact correlated wave functions based on the idea of **electron pairs**, e.g. using **geminals** $\phi_i(\mathbf{x}_1, \mathbf{x}_2)$ instead of orbitals.
- Recent works on systematically approaching FCI (or MCSCF) wave functions by **density-matrix renormalization group (DMRG) method** in which the high-dimensional coefficient tensor in the determinant expansion is decomposed as products of low-dimensional tensors.

For basis convergence and large systems:

- A lot of progress to overcome the slow basis convergence of the post-HF methods by **explicitly correlated methods (or F12 methods)** consisting in extending the virtual space with geminals of the form $f(r_{12})\phi_i(\mathbf{x}_1)\phi_j(\mathbf{x}_2)$ where $f(r_{12})$ is an explicit function of the interelectronic distance r_{12}.
- Active development of **linear-scaling post-HF methods** for large systems by using **localized orbitals** and truncating the number of excitations with a spatial distance criterion.

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Kohn-Sham (KS) density-functional theory (DFT)

- In KS DFT, the **exact energy** is expressed as a minimum over **single-determinant wave functions** Φ:

$$\boxed{E = \min_{\Phi}\left\{ \langle \Phi | \hat{T} + \hat{V}_{\text{ne}} | \Phi \rangle + E_{\text{Hxc}}[n_{\Phi}] \right\}}$$

where $E_{\text{Hxc}}[n_{\Phi}]$ is a **functional of the density** $n_{\Phi}(\mathbf{x}_1) = N \int |\Phi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)|^2 \mathrm{d}\mathbf{x}_2 ... \mathrm{d}\mathbf{x}_N$

- The functional is decomposed as $E_{\text{Hxc}}[n] = E_{\text{H}}[n] + E_{\text{xc}}[n]$ with a **Hartree contribution** $E_{\text{H}}[n] = \dfrac{1}{2} \iint \dfrac{n(\mathbf{x}_1) n(\mathbf{x}_2)}{|\mathbf{r}_2 - \mathbf{r}_1|} \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2$ and an **exchange-correlation contribution** $E_{\text{xc}}[n]$.

- The energy minimization with respect to the spin orbitals leads to the **KS equations**:

$$\boxed{\left(-\frac{1}{2} \Delta_{\mathbf{r}} + v_{\text{ne}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{x}) \right) \psi_i(\mathbf{x}) = \varepsilon_i \psi_i(\mathbf{x})}$$

with the Hartree potential $v_H(\mathbf{r})$ and the exchange-correlation potential $v_{\text{xc}}(\mathbf{x})$

$$v_{\text{H}}(\mathbf{r}) = \int \frac{n(\mathbf{x}')}{|\mathbf{r}' - \mathbf{r}|} \mathrm{d}\mathbf{x}' \quad \text{and} \quad v_{\text{xc}}(\mathbf{x}) = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{x})}$$

and the density $n(\mathbf{x}) = \sum_{i=1}^{N} |\psi_i(\mathbf{x})|^2$.

- **KS DFT is almost as simple as HF** and yet it can in principle give the **exact energy including correlation**. In practice, we need **approximations** for $E_{\text{xc}}[n]$.

Approximations for $E_{\mathrm{xc}}[n]$

- In the **local-density approximation (LDA)**, $E_{\mathrm{xc}}[n]$ is expressed as a **local functional**:

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[n] = \int n(\mathbf{r})\, \epsilon_{\mathrm{xc}}^{\mathrm{unif}}(n(\mathbf{x}))\, \mathrm{d}\mathbf{r}$$

  where $\epsilon_{\mathrm{xc}}^{\mathrm{unif}}(n)$ is the xc energy per particle of the **uniform-electron gas**.

- In the **generalized-gradient approximations (GGA)**, we introduce the density gradient:

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[n] = \int f(n(\mathbf{x}), \boldsymbol{\nabla}_{\mathbf{r}} n(\mathbf{x}))\, \mathrm{d}\mathbf{r}$$

  where f is a function chosen so as to fulfil exact conditions, and often with empirical parameters (Example: BLYP, PBE).

- In the **meta-GGA approximations**, we introduce the density Laplacian and/or kinetic-energy density $\tau(\mathbf{x}) = -(1/2) \sum_{i=1}^{N} |\boldsymbol{\nabla}_{\mathbf{r}} \psi_i(\mathbf{x})|^2$

$$E_{\mathrm{xc}}^{\text{meta-GGA}}[n, \tau] = \int f(n(\mathbf{x}), \boldsymbol{\nabla}_{\mathbf{r}} n(\mathbf{x}), \Delta_{\mathbf{r}} n(\mathbf{x}), \tau(\mathbf{x}))\, \mathrm{d}\mathbf{r}$$

  which constitutes a slight extension of KS DFT (Example: TPSS).

- **Non-local orbital-dependent approximations** involving the orbitals $\psi_i[n](\mathbf{x})$ (and orbital energies $\varepsilon_i[n]$) considered themselves as functionals of the density: exact exchange (EXX), Görling-Levy perturbation theory, random-phase approximation (RPA), ...

WFT+DFT hybrid methods

- In the **multideterminant extension of KS DFT**, the **exact energy** is expressed as a minimum over **multideterminant wave functions** Ψ:

$$E = \min_{\Psi}\left\{\langle\Psi|\hat{T} + \hat{V}_{\text{ne}} + \boldsymbol{\lambda}\hat{W}_{\text{ee}}|\Psi\rangle + \bar{E}^{\boldsymbol{\lambda}}_{\text{Hxc}}[n_\Psi]\right\}$$

with one arbitrary parameter $0 \leq \boldsymbol{\lambda} \leq 1$ and the complement density functional:

$$\bar{E}^{\boldsymbol{\lambda}}_{\text{Hx}}[n] = (1-\boldsymbol{\lambda})E_{\text{Hx}}[n] \quad \text{and} \quad \bar{E}^{\boldsymbol{\lambda}}_{\text{c}}[n] = E_{\text{c}}[n] - \boldsymbol{\lambda}^2 E_{\text{c}}[n_{1/\boldsymbol{\lambda}}]$$

where $n_{1/\boldsymbol{\lambda}}(\mathbf{r}) = (1/\boldsymbol{\lambda}^3)n(\mathbf{r}/\boldsymbol{\lambda})$ is a scaled density.

- Possible approximations for $|\Psi\rangle$:
  - **Single determinant**: $|\Psi\rangle \approx |\Phi\rangle \implies$ **HF+DFT hybrid approximations**:

$$E_{\text{xc}} = \boldsymbol{\lambda}E^{\text{HF}}_{\text{x}}[\Phi] + (1-\boldsymbol{\lambda})E_{\text{x}}[n] + \bar{E}^{\boldsymbol{\lambda}}_{\text{c}}[n]$$

    where $\boldsymbol{\lambda}$ is the fraction of HF exchange (empirically, $\boldsymbol{\lambda} \approx 0.25$). Popular approximations in this family: B3LYP, PBE0.

  - **Single-reference PT** $\implies$ **MP2+DFT double-hybrid approximations**:

$$E_{\text{xc}} = \boldsymbol{\lambda}E^{\text{HF}}_{\text{x}}[\Phi] + \boldsymbol{\lambda}^2 E^{\text{MP2}}_{\text{c}} + (1-\boldsymbol{\lambda})E_{\text{x}}[n] + \bar{E}^{\boldsymbol{\lambda}}_{\text{c}}[n]$$

    which have been actively developed over the last 10 years.

  - **Variational multideterminant wave function**: $|\Psi\rangle = \sum_n c_n|\Phi_n\rangle$ $\implies$ **MCSCF+DFT hybrid approximations**

WFT+DFT range-separated hybrid methods

- An alternative **multideterminant extension of KS DFT** is based on a **range separation** of e-e interaction:

$$E = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{W}_{\mathrm{ee}}^{\mathrm{lr}} | \Psi \rangle + E_{\mathrm{Hxc}}^{\mathrm{sr}}[n_\Psi] \right\}$$

  with a **long-range interaction** $\hat{W}_{\mathrm{ee}}^{\mathrm{lr}} = \sum_{i<j} \frac{\mathrm{erf}(\mu |\mathbf{r}_j - \mathbf{r}_i|)}{|\mathbf{r}_j - \mathbf{r}_i|}$

  a **short-range density functional** $E_{\mathrm{Hxc}}^{\mathrm{sr}}[n]$

  and an arbitrary parameter μ controlling the range of the separation.

- Possible approximations for $|\Psi\rangle$:
  - **Single determinant**: $|\Psi\rangle \approx |\Phi\rangle \Longrightarrow$ **lrHF+srDFT hybrid approximations**:

$$E_{\mathrm{xc}} = E_{\mathrm{x}}^{\mathrm{lr,HF}}[\Phi] + E_{\mathrm{x}}^{\mathrm{sr}}[n] + E_{\mathrm{c}}^{\mathrm{sr}}[n]$$

    Approximations in this family are often referred to as RSH or LC.

  - **Single-reference PT/CC $\Longrightarrow$ lrMP2/lrRPA+srDFT double-hybrid approximations**:

$$E_{\mathrm{xc}} = E_{\mathrm{x}}^{\mathrm{lr,HF}}[\Phi] + E_{\mathrm{c}}^{\mathrm{lr,MP2/RPA}} + E_{\mathrm{x}}^{\mathrm{sr}}[n] + E_{\mathrm{c}}^{\mathrm{sr}}[n]$$

  - **Variational multideterminant wave function**: $|\Psi\rangle = \sum_n c_n |\Phi_n\rangle$ $\Longrightarrow$ **lrMCSCF+srDFT hybrid approximations**

Other DFT-like methods

More simple DFT methods:

- **Density-functional tight binding (DFTB)**: simplified KS-DFT method in which matrix elements are empirically parametrized
  $\Longrightarrow$ useful for large systems
- **Orbital-free DFT**: the total energy is written as a functional of the density without using any orbitals: $E = \min_n E[n]$
  $\Longrightarrow$ appealing but approximations not accurate enough for quantum chemistry

More sophisticated DFT-like methods:

- **Reduced density-matrix functional theory (RDMFT)**: the total energy is written as a functional of the reduced one-particle density matrix $\gamma_1(\mathbf{x}, \mathbf{x}')$: $E = \min_{\gamma_1} E[\gamma_1]$
  $\Longrightarrow$ under active development
- **Variational reduced two-electron density matrix theory**: the total energy is written with the reduced two-particle density matrix $\Gamma_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2')$: $E = \min_{\Gamma_2} E[\Gamma_2]$
  $\Longrightarrow$ natural approach but we do not know the N-representability conditions for the reduced two-electron density matrix Γ_2

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The simplest QMC method: Variational Monte Carlo (VMC)

- **VMC is a method for calculating numerically the multidimensional integrals** of quantum mechanics. For example, for the energy:

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \int d\mathbf{R}\, \Psi(\mathbf{R})^2\, E_\mathrm{L}(\mathbf{R}) \approx \frac{1}{M} \sum_{k=1}^{M} E_\mathrm{L}(\mathbf{R}_k) = \langle E_\mathrm{L} \rangle$$

  where $E_\mathrm{L}(\mathbf{R}) = [H(\mathbf{R})\Psi(\mathbf{R})]/\Psi(\mathbf{R})$ is the **local energy**

  and $\mathbf{R}_k$ are **points randomly sampled from** $\Psi(\mathbf{R})^2$ using the **Metropolis algorithm**.

- According to the central-limit theorem, the **statistical error** on $\langle E_\mathrm{L} \rangle$ is proportional to $\sqrt{V[E_\mathrm{L}]/M}$ where $V[E_\mathrm{L}]$ is the variance of E_L $\Longrightarrow$ **slow decrease** as $1/\sqrt{M}$ but **independent from the number of electrons!**

- **The advantage of VMC is the great flexibility in the form of the wave function** Ψ $\Longrightarrow$ We can use **compact wave functions including weak and strong correlations**, for example:

$$\Psi(\mathbf{R}) = J(\mathbf{R}) \sum_n c_n \Phi_n(\mathbf{R})$$

  where $J(\mathbf{R}) = e^{\sum_{i<j} f(r_{ij})}$ is a **Jastrow factor** depending explicitly on e-e distances and $\Phi_n(\mathbf{R})$ are Slater determinants.

- A lot of on-going work to develop efficient methods to **optimize the wave-function parameters in VMC and calculating properties other than the energy**.

A more sophisticated QMC method: Diffusion Monte Carlo (DMC)

- The **exact ground-state wave function** Ψ_0 can be obtained from an arbitrary starting wave function Ψ (with $\langle \Psi_0 | \Psi \rangle \neq 0$) by using the **imaginary-time evolution operator**:

$$|\Psi_0\rangle \propto \lim_{t \to \infty} e^{-\hat{H}\, t} \, |\Psi\rangle$$

- This is translated in **position space**, after multiplying by $\Psi(\mathbf{R})$, by repeated application of the **importance-sampling Green function** G **for a finite time step** τ:

$$\Psi_0(\mathbf{R})\Psi(\mathbf{R}) \propto \lim_{M \to \infty} \int \mathrm{d}\mathbf{R}_1 ... \mathrm{d}\mathbf{R}_M \; G(\mathbf{R}, \mathbf{R}_M; \tau) \; G(\mathbf{R}_M, \mathbf{R}_{M-1}; \tau) ... G(\mathbf{R}_2, \mathbf{R}_1; \tau) \Psi(\mathbf{R}_1)^2$$

allowing us to use a **short-time approximation to the Green function** G.

- This is realized by a **Metropolis-like algorithm** generating a **weighted random walk** which, after an equilibration phase, samples $\Psi_0(\mathbf{R})\Psi(\mathbf{R}) \approx \sum_{k=1}^{M} w_k \delta(\mathbf{R} - \mathbf{R}_k)$

  In practice, to avoid large variations of the weights, we introduce a **population of walkers performing parallel random walks with a birth-death (or branching) process**. The population size must be controlled to avoid explosion or extinction.

- Knowing $\Psi_0(\mathbf{R})\Psi(\mathbf{R})$, the **exact ground-state energy** E_0 can be calculated as:

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi \rangle = \int \mathrm{d}\mathbf{R} \; \Psi_0(\mathbf{R})\Psi(\mathbf{R}) \; E_\mathrm{L}(\mathbf{R}) \approx \sum_{k=1}^{M} w_k E_\mathrm{L}(\mathbf{R}_k)$$

DMC: The fermion sign problem and the fixed-node approximation

- Because we apply the Green function using finite sampling in position space, the **antisymmetry** of the starting wave function Ψ **is not preserved** during the iterations and we actually converge to the **symmetric bosonic ground-state wave function** Ψ_{B} which has a lower energy than the fermionic ground-state Ψ_0.
  $\Longrightarrow$ This is known as the **fermion sign problem**.

- Even if the antisymmetry is imposed, at any given point $\mathbf{R}$ the algorithm equally samples $+\Psi_0(\mathbf{R})$ and $-\Psi_0(\mathbf{R})$ which gives a zero average $\Longrightarrow$ this is another manifestation of the fermion sign problem.

- To avoid the fermion sign problem, we use the **fixed-node (FN) approximation** corresponding to adding **infinite potential barriers located at the nodes of the starting wave function** (i.e., for $\Psi(\mathbf{R}) = 0$)

  $$H_{\mathrm{FN}}(\mathbf{R}) = H(\mathbf{R}) + \lim_{\lambda \to \infty} \lambda \, \delta(\Psi(\mathbf{R}))$$

  The FN-DMC algorithm then converges to the **FN wave function Ψ_{FN} which is the best variational approximation to Ψ_0 having the same nodes than the approximate Ψ used**.

- Correspondingly, we obtain the **FN energy**: $E_{\mathrm{FN}} = \langle \Psi_{\mathrm{FN}} | \hat{H}_{\mathrm{FN}} | \Psi \rangle = \langle \Psi_{\mathrm{FN}} | \hat{H} | \Psi \rangle \geq E_0$

- Work still needed for calculation of derivatives of E_{FN} for optimization of parameters or for obtaining properties.

Some other QMC methods

- While FN-DMC only samples the mixed distribution $\Psi_{\mathrm{FN}}(\mathbf{R})\Psi(\mathbf{R})$, there are also less used QMC methods sampling the pure distribution $\Psi_{\mathrm{FN}}(\mathbf{R})^2$ such as **reptation quantum Monte Carlo**.

- **Auxiliary-field QMC method**: DMC-like method working in the space of Slater determinants with a fixed-phase approximation

- **FCI-QMC method**: simple DMC-like method working in the space of Slater determinants living with fermion sign problem
  $\Longrightarrow$ a lot of interest since 2009 but exponential scaling computational cost

- Several versions of **stochastic MP2 algorithm**: the Laplace-transform expression of the MP2 correlation energy is evaluated by random sampling
  $\Longrightarrow$ computational cost with a important prefactor but smaller scaling with the system size

A few general references

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