Q&A Session

10 Dec 2024

Written Exam (December) Details

Time & Date & Location

- Written exam will take place on **Monday December 16th**
- We will begin at 10h15 and you will have a full 2 hours to complete the exam
- We'll be in the room by 10h if you'd like to come in early and settle in
- The exam will be held in our usual exercise room **BCH 1103** (where we have interviews)

Materials

- Similar to the first exam you will be allowed written or printed notes on **two separate sheets** of A4 paper each with back and front available
- No calculator will be needed

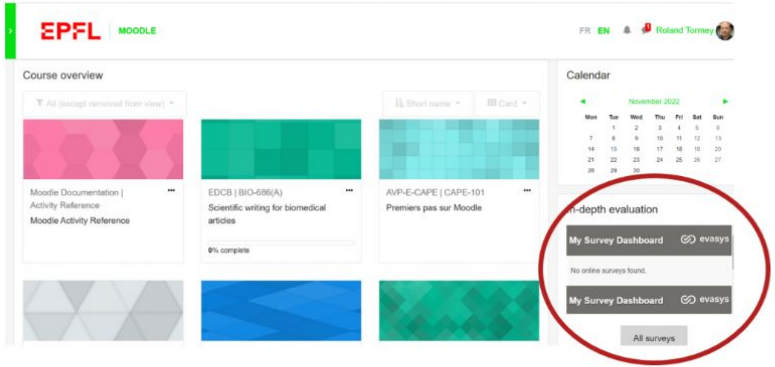
Content

- Chapters 5, 6, 7, 8, Appendix E (**post-HF and DFT** methods) and nothing from chapters 9 or 10

Reminder: In depth evaluation for the course

- Available until 07.01.2025
- How to access the evaluations:
  - Log onto Moodle and stay on the moodle home page (i.e. do not enter the course page)
  - Go to the ‘In-depth evaluation’ box on the right hand side of the moodle home page
  - Select the course and complete the feedback
- Alternatively, via the EPFL Campus App
- Feedback is useful for improving the course especially if the response rate is high. If you can, please take few minutes to fill this in! Thank you!

From EPFL [Teaching support/Resources for students]:



Most of the questions will be objective statements (Likert scale strongly disagree to strongly agree), and you will also have the opportunity to provide some comments. Please note that comments will be most useful if they are respectful and ‘actionable’: a comment which states simply ‘this course is bad’ or ‘this course is great’ is not very helpful; your feedback should indicate what you feel is good about the course and what can be improved.

Feedback Written Exam 1

1. Which of the following operators are i) linear; ii) Hermitian? Explain your reasoning for each case.
   a) the identity operator $\hat{I}$ b) $\sqrt{}$ c) sin d) $\frac{d}{dx}$ e) $x\frac{d}{dx}$ f) $\frac{d}{dx}x$
   g) $\frac{d^2}{dx^2}$ h) the projection operator $\hat{P} = |\varphi_i\rangle\langle\varphi_i|$

2. What are the allowed wavefunctions and corresponding energy eigenvalues for
   a) a particle in a 1D box of length L?
   b) a particle on a ring with circumference L?

3. How many basis functions are included in a calculation of a benzene molecule C_6H_6 (electronic configurations H: $1s^1$; C: $1s^22s^22p^2$) with the basis set 6-31G**? From how many primitive Gaussians is this basis constructed? How much is the computational cost for a Hartree-Fock calculation decreased by using the contracted basis set instead of the primitive Gaussians?

4. What is the general form of a contracted Gaussian basis function? Give a physical motivation why in contracted Gaussian basis sets of the Pople type, s and p shells with the same principal quantum number share the same exponents but differ in their coefficients.

5. Calculate the ionization energy $IE = E(N) - E(N-1)$ where N is the total number of electrons using the Hartree-Fock energy expression
   $E_{HF} = \sum_i \langle i | \hat{h} | i \rangle + \frac{1}{2}\sum_{ij}([ii|jj] - [ij|ji])$ assuming that the Fock orbitals do not change upon the removal of an electron. How is this result related to the Hartree-Fock orbital eigenvalues?

6. You are performing an unrestricted Hartree-Fock calculation of a system with a a) singlet; b) doublet and c) triplet ground state. The expectation values of the S^2 operator that you obtain are a) 2.0; b) 0.75 and c) 2.1. What do you conclude and recommend from that for each case?

Bonus: What is the counterpoise correction? When is it important?

1. Mostly good answers, but most students got wrong answer for d/dx operators

2. Question more difficult, most students couldn't write the correct wavefunction for a) and b). But some good attempts at defining boundaries, allowed quantum number, periodicity …

3. Overall well answered. Remember: scaling N^4 and count polarisation functions as CGTO

4. Most answers were partially correct. Share the same exponents because exponent determines average distance of electron from nuclei

5. Overall well answered. Remember: don't add a ½ as a coefficient to the (J+K) term, and merge 2 terms

6. Heterogeneous. Important to know how to calculate multiplicity and $\langle S^2 \rangle = S(S+1)$ (singlet, S=0, $\langle S^2 \rangle = 0$)

Bonus. Most answers were very good, but some students didn't explain when counterpoise correction is important

Overview Slide

Some important features of electronic structure methods:

- What is the Ansatz for the wavefunction?
- How are exchange and correlation treated?
- Can static correlation/multireference problems be treated?
- Is the method variational (i.e. is E always ≥ E_true)?
- Is the method size consistent (i.e. is the energy of two non-interacting systems the sum of the single systems?)
- Can excited states be treated with the same method?
- What is the scaling of the method (i.e. how does the computational cost grow if I double the system size?)

Method	wavefunction	exchange	correlation	variational?	Size-consistentt?	multi-ref?	Excited states?	Scaling
HF	1 determinant	exact	none	yes	yes	no	no	N^2-N^4
MPn	contributions from excited determinants through perturbation	exact	some	no	yes	CAS-PT2	CAS-PT2	MP2 N^5 MP3 N^6 MP4 N^7
Truncated CI	selected determinants	exact	some	yes	no	no	yes	e.g. CISD N^6
CASSCF	selected dets determinants	exact	little	yes	no	yes	yes	exp, N_{act}*N_{det}^4
CC	contribution of selected excitations through infinite order	exact	some	no	yes	no	EOM-CC CC2	CCSD N^6 CCSD(T) N^7 CCSDT N^8 CCSDTQ N^{10}
Full CI	exact wf within basis set, linear combination of all possible excited determinants	exact	all	yes	yes	yes	yes	$N!/N_{el}!(N-N_{el})!$
Exact DFT	electron density	exact	exact	yes	yes	no	TDDFT	N
Orbital-free DFT	electron density	some	some	no	yes	no	TDDFT	N
KS-DFT	electron density	some	some	no	yes	no	TDDFT	N^2-N^3

Mock Exam

1. What is meant by the term correlation hole?
2. Name two ways of how to reduce the number Slater determinants in configuration interaction when treating a) dynamic correlation and b) static correlation.
3. Which methods do have a possible self-interaction (i.e. an electron interacting with itself) error: a) CISD; b) MP2; c) CCCSD(T) and d) KS-DFT with approximate exchange-correlation functional.
4. a) What is the energy correction due to electron correlation at a) first-order (MP1)? b) Derive the expression for the energy correction at 2nd order (MP2).
5. What is the wavefunction Ansatz in coupled cluster theory? Using the same one-electron basis set e.g. 6-3111+G**, which method is more accurate: CISD or CCSD? Why?
6. Write down the relation between the many-electron wavefunction and the electron density. Can you determine the ground state electron density via a variational principle in a) exact DFT? b) DFT with an approximate exchange-correlation functional? Why? Is the resulting ground state energy above or below the exact value?

Bonus: What are generalized gradient approximations (GGAs)? Why are they called 'generalized'? Give a few examples of frequently used GGA.

Mock Exam Question 1

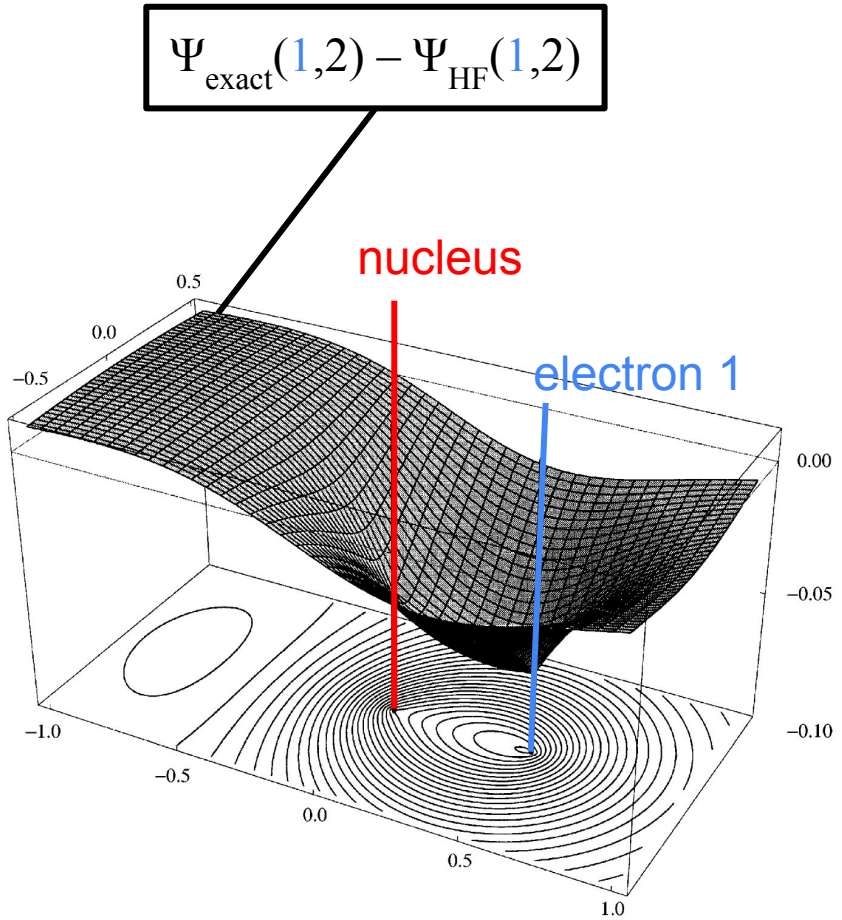
What is meant by the term correlation hole?

Two electrons repulse themselves due to the instantaneous Coulomb interaction
→ their motion is correlated

Example: **Helium atom**

The surface represents a difference between exact and HF wave functions as a function of **electron 2** coordinates while **electron 1** is at a fixed position.

A drop around the position of **electron 1** represents a decrease in probability of finding the **electron 2** in its vicinity → repulsion



Mock Exam Question 2

Name two ways of how to reduce the number Slater determinants in configuration interaction when treating a) dynamic correlation and b) static correlation.

Mock Exam Question 2

Name two ways of how to reduce the number Slater determinants in configuration interaction when treating a) dynamic correlation and b) static correlation.

a) → We can limit the maximum excitation rank… → e.g. CISD

$$|\Psi_{\text{CISD}}\rangle = C_0|\Phi_0\rangle + \sum_{ar} C_a^r|\Phi_a^r\rangle + \frac{1}{2}\sum_{abrs} C_{ab}^{rs}|\Phi_{ab}^{rs}\rangle + \frac{1}{6}\sum_{abcrst} C_{abc}^{rst}|\Phi_{abc}^{rst}\rangle + \cdots$$

b) → …or the orbital space in which we perform excitations → CAS-CI

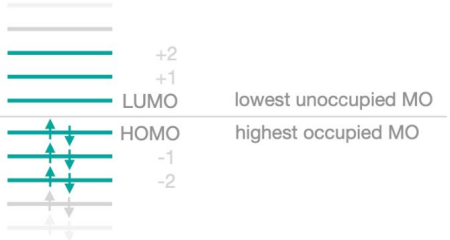
$$|\Psi_{\text{CAS-CI}}\rangle = C_0|\Phi_0\rangle + \sum_{ar} C_a^r|\Phi_a^r\rangle + \frac{1}{2}\sum_{abrs} C_{ab}^{rs}|\Phi_{ab}^{rs}\rangle + \frac{1}{6}\sum_{abcrst} C_{abc}^{rst}|\Phi_{abc}^{rst}\rangle + \cdots$$

$$a, b, c\ldots \in \{1, 2\ldots, H-2, H-1, H\}$$

$$r, s, t\ldots \in \{L, L+1, L+2, \ldots N-1, N\}$$

HOMO

LUMO



Mock Exam Question 3

Q: Which methods do have a possible self-interaction (i.e. an electron interacting with itself) error: a) CISD; b) MP2; c) CCSD(T) and d) KS-DFT with approximate exchange-correlation functional.

Mock Exam Question 3

Q: Which methods do have a possible self-interaction (i.e. an electron interacting with itself) error: a) CISD; b) MP2; c) CCSD(T) and d) KS-DFT with approximate exchange-correlation functional.

A: Self interaction can arise from energy terms involving two-electron

- In HF, we saw self-interaction cancels out explicitly (for electron *a*, $J_{aa}=K_{aa}$)
- In the post-HF method listed, there is no term really involving one electron and the interaction with itself, e.g. in MP2

$$E(\mathrm{MP2}) = \sum_{a<b}^{\mathrm{occ.}} \sum_{r<s}^{\mathrm{virt.}} \frac{\left[\langle \phi_a \phi_b | \hat{v} | \phi_r \phi_s \rangle - \langle \phi_a \phi_b | \hat{v} | \phi_s \phi_r \rangle\right]^2}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)}$$

Note: if *a* and *b* could be equal (even if this would not correspond to a self-interaction as in HF), those terms would cancel out

- In DFT, on the other side, we always have Coulomb terms where electron density can interact with itself. The energy is a functional of the single-particle density, so there is no way to precisely distinguish two-body Coulomb interactions from self-interaction. One therefore includes the interaction of each electron with the entire electron density (including its own density).

$$E_0 = \sum_{i=1}^{N} \varepsilon_i - \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho_0(\mathbf{r})\rho_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \int d^3r v_{xc}(\mathbf{r})\rho_0(\mathbf{r}) + E_{xc}[\rho_0]$$

self-interaction-corrected correlation functional exist !

Mock Exam Question 4

What is the energy correction due to electron correlation at a) first-order (MP1)? b) Derive the expression for the energy correction at 2nd order (MP2).

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$$\hat{H} = \hat{H}_0 + \lambda \hat{V}.$$

unperturbed Hamiltonian

perturbation

time-independent Schrödinger equation

$$\left(\hat{H}_0 + \lambda V\right)\left(\sum_{i=0}^{m} \lambda^i \Psi^{(i)}\right) = \left(\sum_{i=0}^{m} \lambda^i E^{(i)}\right)\left(\sum_{i=0}^{m} \lambda^i \Psi^{(i)}\right).$$

$$\Psi = \lim_{m\to\infty} \sum_{i=0}^{m} \lambda^i \Psi^{(i)},$$

$$E = \lim_{m\to\infty} \sum_{i=0}^{m} \lambda^i E^{(i)}.$$

$$\hat{H}_0 \equiv \hat{F} + \langle \Phi_0 | (\hat{H} - \hat{F}) | \Phi_0 \rangle$$

$$\hat{V} \equiv \hat{H} - \hat{H}_0 = \hat{H} - \left(\hat{F} + \langle \Phi_0 | (\hat{H} - \hat{F}) | \Phi_0 \rangle\right)$$

Mock Exam Question 4

the first meaningful correction appears at MP2 energy.

$$E_{\mathrm{MP1}} \equiv \langle \Phi_0 | \hat{V} | \Phi_0 \rangle = 0.$$

What is the energy correction due to electron correlation at a) first-order (MP1)? b) Derive the expression for the energy correction at 2nd order (MP2).

a) $$E^{(0)} = \sum_i^N \langle \phi_i | \hat{\mathcal{F}}_i | \phi_i \rangle \ , \ E^{(1)} = \langle \Phi_0 | \mathcal{H}' | \Phi_0 \rangle \longrightarrow \mathrm{MP1}: \quad E(\mathrm{MP0}) + E(\mathrm{MP1})$$

b) $$(\mathcal{H}^{(0)} + \lambda \mathcal{H}')(\lambda^0 \Psi^{(0)} + \lambda^1 \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \dots) =$$

$$(\lambda^0 E^{(0)} + \lambda^1 E^{(1)} + \lambda^2 E^{(2)} + \dots)\,(\lambda^0 \Psi^{(0)} + \lambda^1 \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \dots)$$

$$\lambda^{(2)}: \mathcal{H}^{(0)}\,\Psi^{(2)} + \mathcal{H}'\Psi^{(1)} = E^{(0)}\,\Psi^{(2)} + E^{(1)}\,\Psi^{(1)} + E^{(2)}\,\Psi^{(0)}$$

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

Mock Exam Question 4

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What is the energy correction due to electron correlation at a) first-order (MP1)? b) Derive the expression for the energy correction at 2nd order (MP2).

$$H_0\Psi_0 = E^{(0)}\Psi_0$$

$$H_0\Psi^{(1)} + V\Psi_0 = E^{(0)}\Psi^{(1)} + E^{(1)}\Psi_0$$

$$H_0\Psi^{(2)} + V\Psi^{(1)} = E^{(0)}\Psi^{(2)} + E^{(1)}\Psi^{(1)} + E^{(2)}\Psi_0$$

$$E^{(0)} = \langle \Psi_0 | H_0 | \Psi_0 \rangle$$

$$E^{(1)} = \langle \Psi_0 | V | \Psi_0 \rangle$$

$$E^{(2)} = \left\langle \Psi_0 | V | \Psi^{(1)} \right\rangle$$

Hartree-Fock energy

$$E_0 = \langle \Psi_0 | H_0 + V | \Psi_0 \rangle = E^{(0)} + E^{(1)}$$

correlation energy

$$E_{\mathrm{corr}} = E_0^{(2)} + E_0^{(3)} + E_0^{(4)} + \ldots$$

MP2 energy

Mock Exam Question 5

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$$|\Psi\rangle = e^{\hat{T}}|\Phi_0\rangle \quad e^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \cdots = 1 + \hat{T}_1 + \hat{T}_2 + \frac{\hat{T}_1^2}{2!} + \hat{T}_1\hat{T}_2 + \frac{\hat{T}_2^2}{2!} + \ldots$$

CCSD accounts for some triple and quadruple excitations by approximating them as products of single and double excitation.

https://doi.org/10.1016/S0065-3276(08)60532-8

Mock Exam Question 6

Write down the relation between the many-electron wavefunction and the electron density. Can you determine the ground state electron density via a variational principle in a) exact DFT? b) DFT with an approximate exchange-correlation functional? Why? Is the resulting ground state energy above or below the exact value?

Mock Exam Question 6

Write down the relation between the many-electron wavefunction and the electron density. Can you determine the ground state electron density via a variational principle in a) exact DFT? b) DFT with an approximate exchange-correlation functional? Why? Is the resulting ground state energy above or below the exact value?

$$\rho(\mathbf{r}) = M \int \cdots \int \Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)\, \Psi^*(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)\, d\mathbf{r}_2 \ldots d\mathbf{r}_N$$

a) Yes. We can look at the second HK (Hohenberg-Kohn) theorem: it defines an energy functional for the system and proves that the ground-state electron density minimizes this energy functional.

$$E_v[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V}_{eN} | \Psi \rangle$$

If $\rho(r) \neq \rho_0(r)$ then $\Psi \neq \Psi_0$ and $E_v > E_0$

b) No guarantee. The expression of the energy based on electron-density introduces approximations for the exchange-correlation energy term. In this way, the use of the approximate functional could result in an energy limit which is below the exact ground state energy value.

Mock Exam Bonus

Bonus: What are generalized gradient approximations (GGAs)? Why are they called ‘generalized’? Give a few examples of frequently used GGA.

Mock Exam Bonus

The GGA add a term reflecting a gradient of electron density at a given point, accounting in part for an inhomogeneous distribution of electron density and some non-local effects.

Bonus: What are generalized gradient approximations (GGAs)? Why are they called ‘generalized’? Give a few examples of frequently used GGA.

$$E_{xc}^{GGA}[\rho] = \int d^3 f\left(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})\right)$$

where function, f, can take different forms. Instead of power-series-like systematic gradient expansions one could experiment with **more general functions** of both the electron density and its gradient. For example from the slides here’s one such function:

$$F_x^{B88}(s) = 1 + \frac{\gamma c_2 c_1^2 s^2}{1 + 6\gamma c_1 s \sinh^{-1}(c_1 s)} \qquad s = \frac{|\nabla\rho(\vec{r})|}{\rho(\vec{r})}$$

Reduced gradient

PBE, BLYP, and B88 are common GGA functionals.

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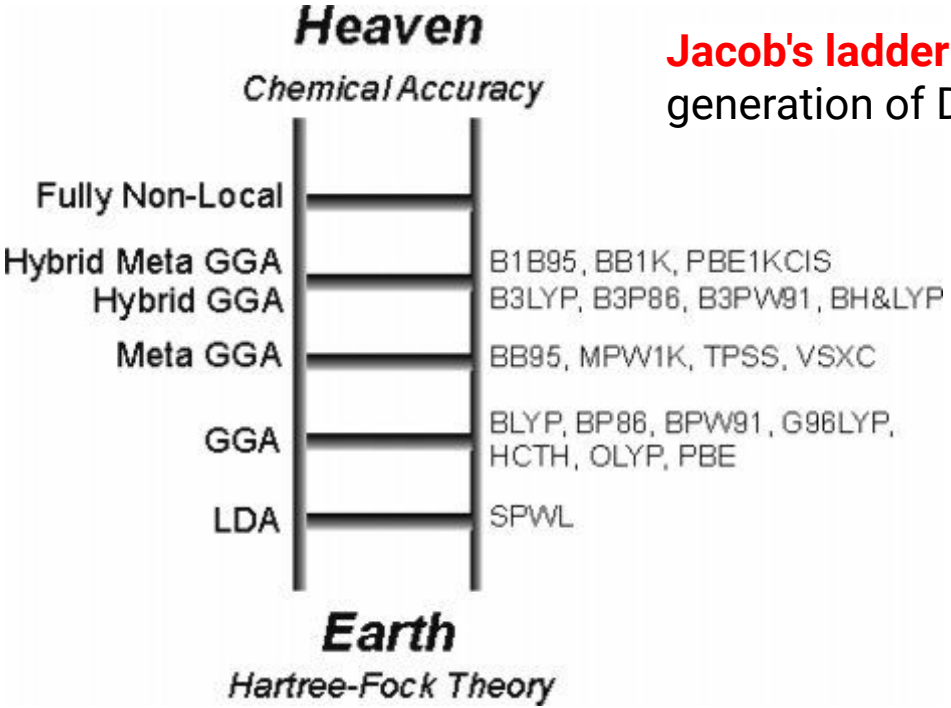
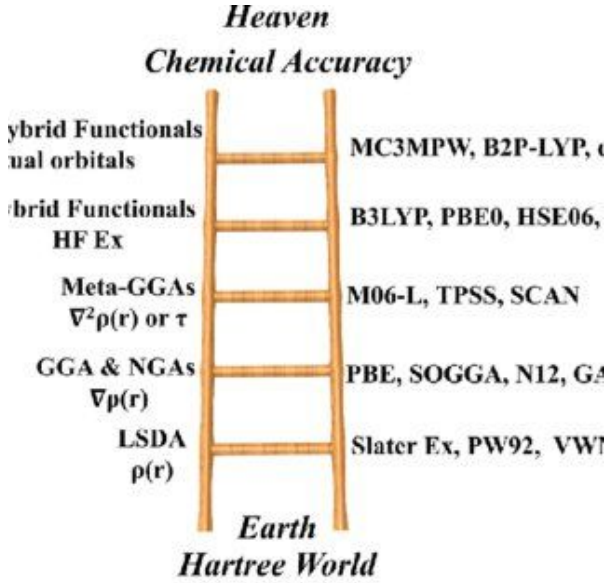


Jacob's ladder for the five generation of DFT functionals



Question from Student

One question regarding the way Löwdin expressed the electron correlation on slide - could you clarify the signs of the energy values?

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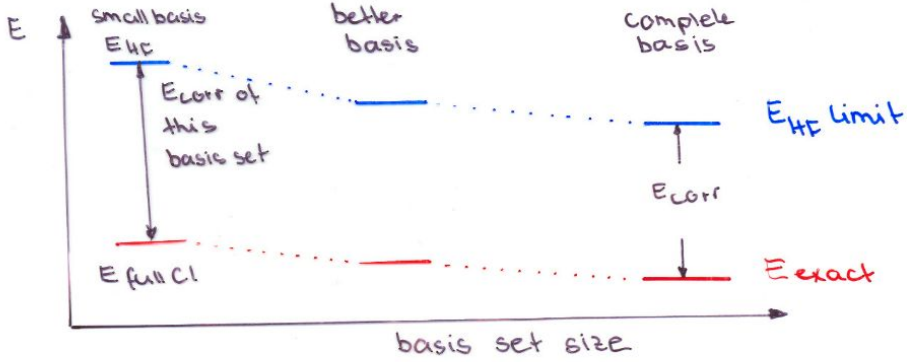
When correlation energy is included, the total calculated energy of the system is lower (more negative) than just the energy recovered from HF.

Chemist's definition of E_{corr} (Lowdin):

$$E_{exact}^{nonrel} = E_{HF_{limit}} - E_{corr}$$



$\rightarrow E_{corr}$ **is basis set dependent!**

$$E_{corr} = E_{exact} - E_{HF}$$

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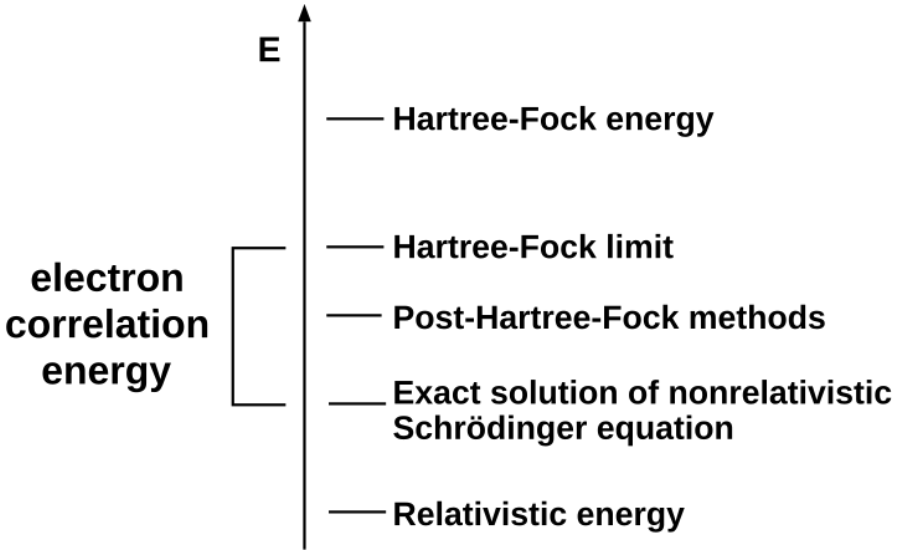

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Q: What is the difference between exchange energy and correlation energy?

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A: In the context of DFT, the exchange-correlation energy term is often decomposed into exchange energy and correlation energy

$$E_{xc} = E_x + E_c$$

This distinction is quite arbitrary, but the idea to include in the exchange term (E_x) effects due to the Pauli principle, and in the correlation term (E_c) effects due to electron-correlation.

In KS DFT with approximated functionals, different functional forms are assumed for E_{xc}, or for E_x and E_c.

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Could you clarify which post-HF methods, including DFT, recover dynamic and/or static correlation?

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Could you clarify which post-HF methods, including DFT, recover dynamic and/or static correlation?

- All of the post-HF methods+DFT capture some electron correlation.
- FCI is exact thus it will recover all correlation same as untruncated CC. Exact DFT also recovers all correlation as the exact ground state energy depends only on the ground state electron density.
- As dynamic correlation is present in all systems, each of these methods will aid in recovering dynamic correlation.
- Multiconfigurational methods like CASSCF explicitly account for static correlation unlike truncated, single reference methods like CISD

Review Material

Ch 5 - Configuration Interaction

Ch 6 - Perturbation Theory

Ch 7 - Coupled Cluster

Ch 8 - Density Functional Theory

Appendix E - Multiconfigurational Methods

(Ch 9 & Ch 10 - Not tested!)

Ch 5 - Configuration Interaction (5.1-5.2)

From here on out we're hoping to improve on the HF calculations:

- CI improves on HF by providing a set of "infinite" Slater determinants instead of just one. We expand our wavefunction into a complete basis set $\{\Phi_i\}$
- If we have a true complete basis set of one-electron spin orbitals, then we will have infinite possible N-electron basis functions which can be written as excitations from the HF "reference" Slater determinant:

$$|\Psi\rangle = c_0|\Phi_0\rangle + \sum_{ra} c_a^r|\Phi_a^r\rangle + \sum_{a<b,r<s} c_{ab}^{rs}|\Phi_{ab}^{rs}\rangle + \sum_{r<s<t,a<b<c} c_{abc}^{rst}|\Phi_{abc}^{rst}\rangle + \dots \quad (5.3)$$

- Every N-electron Slater determinant is a configuration and therefore the configuration interaction is the matrix solution of contributing configurations
- Incomplete 1-e basis means complete CI impossible. Full CI (FCI) is the solution exactly within space of specific basis, but usually we do a truncated CI, like CISD, or active space CI, like CASCI.

Ch 5 - Configuration Interaction (5.3) - Correlation Energy

- With CI we see a recovery of correlation energy absent in HF:
  - $E_{corr} = E_{exact} - E_{HF}$

- Electron correlation is customarily divided into dynamic and static (non-dynamic). There is no strict definition of these terms, but…
  - **Dynamic**:
    Electrons experience instantaneous repulsions from other electrons as they move

  - **Static**:
    Near-degeneracies at the ground state → a single reference configuration is inadequate to describe the ground state

Ch 5 - Configuration Interaction (5.6)

- Slater-Condon rules or how to build a CI Hamiltonian matrix
  - Recall H matrix is the matrix representation of the Hamiltonian operator in a given N-electron basis with the element H_{ij} being equal to $\langle \boldsymbol{\Phi}_i \, | \boldsymbol{\mathcal{H}} | \, \boldsymbol{\Phi}_j \rangle$
  - Read section 5.4 and understand these are all 1 or 2 electron integrals which form H matrix
  - We have to arrange 2 Slater det in maximum coincidence, getting them to look similar
  - **Four Rules**: Identical, One Difference, Two Differences, 3+ Differences (zero)
- Matrix elements of single excitations from reference are zero (Brillouin's theorem). The matrix element between 2 Slater determinants differing by 1 spin orbital is an off-diagonal Fock matrix element in HF (zero by definition).

$$\mathbf{H} = \begin{array}{c} \langle \Phi_0 | \\ \langle S | \\ \langle D | \\ \langle T | \\ \langle Q | \\ \vdots \end{array} \begin{bmatrix} \langle \Phi_0 | H | \Phi_0 \rangle & & & & & & \cdots \\ 0 & \langle S | H | S \rangle & & & & & \cdots \\ \langle D | H | \Phi_0 \rangle & \langle D | H | S \rangle & \langle D | H | D \rangle & & & & \cdots \\ 0 & \langle T | H | S \rangle & \langle T | H | D \rangle & \langle T | H | T \rangle & & & \cdots \\ 0 & 0 & \langle Q | H | D \rangle & \langle Q | H | T \rangle & \langle Q | H | Q \rangle & & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix}$$

Ch 5 - Configuration Interaction

CI is usually truncated to single and double excitations (CISD). Double excitations make biggest CI contributions.

The **size of the N-electron basis** (Slater determinants) depends on the **size of the 1-electron basis** (basis functions (e.g. 6-311G*)).

$$\#SD = \frac{N_{bas}!}{N_{el}!\,(N_{bas} - N_{el})!}$$

Pros

- Can apply CI to excited states, open shell, non-equilibrium states
- Can provide the exact matrix solution of the time-independent non-relativistic electronic Schrödinger equation
- CISD can capture ~95% correlation energy for small molecules near equilibrium
- Is variational

Cons

- Computationally intractable to perform FCI for anything but tiny systems because of the number of slater determinants
- Not size extensive or size consistent for truncated CI (but it is for CASCI if you define your active space properly)

Ch 6 - Perturbation Theory (6.1 - 6.1.2)

- General perturbation theory

  $\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}' \rightarrow \lambda$ *parameter determining strength of perturbation, between 0-1*

- Zero-order (unperturbed): $\lambda^0 = 1$; $\hat{H} = \hat{H}^{(0)}$; $\Psi^{(0)} = \Phi_0$; $E^{(0)} = E_0$
- First-order → nth order (perturbed):
  - Expand into power series around λ
  - Define the first, second…nth order *correction* values for energy and wavefunctions $E^{(1)}$, $E^{(2)}$...$E^{(n)}$
- **Normalize**: correction terms orthogonal to $\Psi^{(0)}$ meaning $\langle \Psi^{(i \neq 0)} | \Phi \rangle = 0$
- Apply correction terms to Schrodinger's Equation

  $(\hat{H}^{(0)} + \lambda \hat{H}')(\lambda^0 \Psi^{(0)} + \lambda^1 \Psi^{(1)} + \lambda^2 \Psi^{(2)} + ...) = (\lambda^0 E^{(0)} + \lambda^1 E^{(1)} + \lambda^2 E^{(2)} + ...)(\lambda^0 \Psi^{(0)} + \lambda^1 \Psi^{(1)} + \lambda^2 \Psi^{(2)} + ...)$
  - Collect terms of similar powers in perturbation equations:
    - For $\lambda^2 \rightarrow \hat{H}^{(0)} \Psi^{(2)} + \hat{H}' \Psi^{(1)} = E^{(0)} \Psi^{(2)} + E^{(1)} \Psi^{(1)} + E^{(2)} \Psi^{(0)}$
    - For $\lambda^n \rightarrow \hat{H}^{(0)} \Psi^{(n)} + \hat{H}' \Psi^{(n-1)} = \sum E^{(j)} \Psi^{(n-j)}$ from $j = 1$ to $j = n$

Ch 6 - Perturbation Theory (6.1.3 - 6.2)

- Expand wavefunction corrections into complete set of orthogonal functions (Rayleigh-Schrödinger perturbation theory). Example: First order Perturbation

$$(\hat{H}^{(0)} - E^{(0)})\Psi^{(1)} + (\hat{H}' - E^{(1)})\Phi^{(0)} = 0 \text{ where } \Psi^{(1)} = \sum c_i \Phi_i \text{ from } i = 0 \text{ to } i = \infty$$

$$\text{For a given } i = j \rightarrow c_j = \frac{\langle \Phi_j | \hat{H}' | \Phi_0 \rangle}{(E_0 - E_j)}$$

- Expansion coefficients determine corrections to perturbed wavefunction
- Corrections are expressed in matrix elements of perturbation Hamiltonian, $\hat{H}'$, over the unperturbed wavefunctions and energies
- Ok, so how do we actually perform perturbation theory? **Møller-Plesset!**

$\hat{H}^{(0)}$**:** Sum of single particle Fock Operators (HF)
$\hat{H}'$**:** Difference between full Hamiltonian and HF Hamiltonian $r^{-1} - v_{HF}$

Ch 6 - Perturbation Theory (6.2 continued)

- $\hat{H}^{(0)}$ requires use of Fock Operators (*i* and *j* are electron indices):

$$F_i = h_i + \sum (\hat{J}_i - \hat{K}_i) \text{ from } j \text{ to } N \quad \text{where we know} \quad \hat{F}_i \Phi_i(x_i) = \varepsilon_i \Phi_i(x_i)$$

- Take Fock operator for an unperturbed Hamiltonian, $\hat{H}^{(0)}$

$$\hat{H}^{(0)} = \sum_{i=1}^{N} \hat{F}_i = \sum_{i=1}^{N} \hat{h}_i + \sum_{i=1}^{N} \sum_{j=1}^{N} (\hat{J}_{ij} - \hat{K}_{ij})$$

- Rearrange to find the $\hat{H}'$ operator: $\hat{H}' = \hat{H}^{FULL} - \hat{H}^{(0)} = \sum_{i<j}^{N} \hat{\boldsymbol{v}}_{ij} - \sum_{i,j=1}^{N} \hat{v}_{ij}^{HF}$
- If you do the math, you'll see we're double counting e-e repulsion at zero order BUT the first order energy ($E^{(0)}+E^{(1)}$) is exactly the HF energy!
- Therefore, so in MPn, correlation energy matters at orders of 2+

Ch 6 - Perturbation Theory (6.2 continued)

- Solutions to unperturbed problem should be infinite, but truncated in practice
  - Unperturbed state = HF wavefunction. Higher energy solutions = excited Slater determinants
- Singly excited Slater determinants don't contribute to energy (Brillouin)
- Doubled excited Slater determinants → promote 2 electrons from occ orbitals to unocc. Organize summation so only counting each excited state once:

$$E^{(2)} = \sum_{a<b}^{\text{occ.}} \sum_{r<s}^{\text{virt.}} \frac{\langle \Phi_0 | \hat{\mathcal{H}}' | \Phi_{ab}^{rs} \rangle \langle \Phi_{ab}^{rs} | \hat{\mathcal{H}}' | \Phi_0 \rangle}{E_0 - E_{ab}^{rs}}$$

$$E(\text{MP2}) = \sum_{a<b}^{\text{occ.}} \sum_{r<s}^{\text{virt.}} \frac{\left[\langle \phi_a \phi_b | \hat{v} | \phi_r \phi_s \rangle - \langle \phi_a \phi_b | \hat{v} | \phi_s \phi_r \rangle \right]^2}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)}$$

Ch 6 - Perturbation Theory (6.2 continued)

Pros

- MP2 is a N^5 method because it's the sum of two 2-election integrals plus transformation integrals from AO to MO. Still *decently* cheap and gets 80-90% correlation energy typically.

Cons

- Must have a good zeroth-order wavefunction so the assumption that the perturbation is small is a good one. HF needs to be a decent starting point.
- Difficult to prove perturbation expansion is convergent (basis set dependence). So in practice only low orders of perturbation are carried out, usually landing on MP2 even though it often overshoots correlation energy.

Ch 7 - Coupled Clusters (7.1)

Key Points to Note From Extra Textbook Info

- Size Extensivity vs. Size Consistency
  - **Extensivity**: energy should scale linearly with system size
  - **Consistency**: can break up the Hamiltonian per system part *E(AB) = E(A) + E(B)*
- CC includes all corrections of a given type (S,D,T, etc) to infinite order
- Comprised of an exponential ansatz with a cluster operator $\mathcal{T}$. The $\mathcal{T}$ operator produces a linear combination of excited state Slater determinants

$|\Psi\rangle = e^{\mathcal{T}}|\Phi_0\rangle$ where $\mathcal{T} = \mathcal{T}_1 + \mathcal{T}_2 + \ldots$ and $\mathcal{T}_1 \rightarrow$ operator for all single excitations

- $\mathcal{T}$ operators are composed of creation and annihilation operators between occupied and unoccupied orbitals
- We must solve for unknown *t* coefficients

Ch 7 - Coupled Clusters (7.2-7.4)

- We can define an expression for energy depending on our choice of where to truncate excitations. Example with singles and doubles

$$E_{cc} = E_0 + \sum_{a}^{\text{occ}} \sum_{r}^{\text{vir}} t_a^r \langle \Phi_0 | \hat{H} | \Phi_a^r \rangle + \sum_{ab(a<b)}^{\text{occ}} \sum_{rs(r<s)}^{\text{vir}} (t_{ab}^{rs} + t_a^r t_b^s - t_a^s t_b^r) \langle \Phi_0 | \hat{H} | \Phi_{ab}^{rs} \rangle$$

- If we use HF orbitals for the Slater determinant then the contributions from singly excited determinants are zero (Brillouin)
- There are formulas to solve for *t* coefficients → amplitude equations
- CCSDT vs CCSD(T)
  - CCSDT includes $\mathcal{T}$ operators for single, double, and triple excitations
  - CCSD(T) includes $\mathcal{T}$ operators for single and double excitations. Triples are treated with perturbation theory like we observed in MPn methods

Ch 7 - Coupled Clusters

Pros - CC theory preferred over the CI and MP methods for the following reasons:

- It is size-extensive
- It can be size-consistent if the reference wavefunction is size-consistent
- It provides fast and systematic convergence to the full CI solutions
- When truncated, CC usually recovers more correlation energy than CI because of the inclusion of higher excitations

Cons

- CC energy is not variational
- Computational cost scales steeply with the size of the system

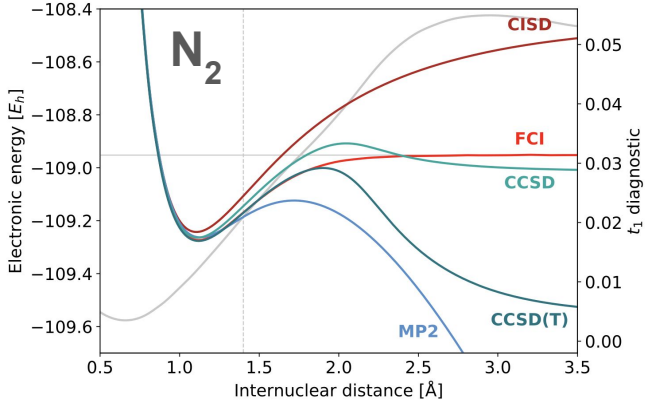
Appendix E - Multiconfigurational methods

Systems with static correlation → single determinantal wave functions inadequate

- dissociations, transition metals, excited states…

Complete active space (CAS) methods provide a cheaper alternative to Full CI and capture static corr.

We can optimize the wave function using the MCSCF methods such as CASSCF



Dynamic correlation is still important!!! → multireference CI, MBPT, CC…

CAS selection is non-trivial and requires a certain insight into the investigated problem → bonding/antibonding pairs for dissociation, unsaturated planar π/π*, ...

Ch 8 - Density Functional Theory (DFT)

Hohenberg–Kohn theorems:

1) The ground state wavefunction is a unique functional of ground state density

$$\Psi_0(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \Psi[\rho_0(\mathbf{r})]$$

- $O_0 = O[\rho_0] = \langle \Psi[\rho_0] | \hat{O} | \Psi[\rho_0] \rangle$
- $E_{v,0} = O[\rho_0] = E_v[\rho_0] = \langle \Psi[\rho_0] | \hat{H} | \Psi[\rho_0] \rangle$

2) Variational principle: for any density ρ'

$$E_v[\rho_0] \leq E_v[\rho'] \qquad \text{where == ONLY IF } \rho' = \rho_0$$

$$E_{v,0} = E_v[\Psi_0] = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \leq \langle \Psi' | \hat{H} | \Psi' \rangle = E_v[\Psi']$$

Ch 8 - Exact DFT

From HK theorems we have a recipe to calculate all the ground state properties, by performing a 3 dimensional minimization (the wavefunction analogue requires 3N dimensional minimization!)

$$E_v[\rho] = T[\rho] + V_{ee}[\rho] + V_{eN}[\rho] \ , \quad \frac{\delta E_v[\rho]}{\delta \rho(\mathbf{r})} = 0 \rightarrow \rho_0 \Rightarrow E_{v,0} \text{ and any } O[\rho_0]$$

BUT expressions for T, V_{ee}, and V_{eN} are needed ⇒ approximations

- Thomas-Fermi approach: example of exact DFT (KS DFT precursor)

$$E[\rho] = T[\rho] + V_{ee}[\rho] + V_{eN}[\rho] \approx E^{TF}[\rho] = T_s^{LDA}[\rho] + V_H[\rho] + V_{eN}[\rho]$$

$$T[\rho] \approx T^{LDA}[\rho] \approx T_s^{LDA}[\rho] = \int t_s^{hom}(\rho(\mathbf{r}))d^3r$$

homogeneous system

noninteracting system

known exactly:

$$t_s^{hom}(\rho) = 3\hbar^2(3\pi^2)^{2/3}\rho^{5/3}/(10m_e)$$

$$V_{ee} \approx V_H = \frac{1}{2}\int d^3r \int d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Ch 8 - Kohn-Sham DFT

TF approximation for T is not accurate. It is possible to separate T[ρ]

$T[\rho] = T_s[\rho] + T_c[\rho]$, expression for T_s for not known as a functional of ρ, but known exactly for single-particle orbitals of a noninteracting system with density ρ

$$T_s[\rho] = -\frac{1}{2}\sum_i^N \int d^3r\, \phi_i^*(\mathbf{r})\nabla^2\phi_i(\mathbf{r}) \quad \Rightarrow \quad E[\rho] = T_s[\{\phi_i[\rho]\}] + V_H[\rho] + E_{xc}[\rho] + V_{eN}[\rho]$$

Indirect minimization considering an auxiliary noninteracting system with same density, under the influence of an external potential $v_s(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$
$\Rightarrow \rho_s(\mathbf{r}) \equiv \rho(\mathbf{r})$ by solving (SCF!) Kohn-Sham equations: $\left[-\frac{\nabla^2}{2} + v_s(\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$

- So far theory is exact, BUT expression for $v_{xc}(\mathbf{r})$ not known ⇒ approximations
- "Koopman's theorem" for KS DFT, for exact case: $\varepsilon_{N+1}(N+1) = -A$, $\varepsilon_N(\bar{M}) = -I$

Ch 8 - Functionals

Types of $E_{xc}[\rho]$ Approximations

virtual ϕ_i — Double hybrids

Exact HF exchange Occupied ϕ_i — hybrids, meta hybrids → fraction of HF exchange energy

$\rho(\vec{r}), \nabla\rho(\vec{r}), \tau(\vec{r}) = \frac{1}{2}\sum_i \left|\nabla\phi_i(\vec{r})\right|^2$ — meta

KS kinetic energy

$$E_{xc}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \tau(\mathbf{r})]$$

$\rho(\vec{r}), \nabla\rho(\vec{r})$ — GGAs

$$E_{xc}^{GGA}[\rho] = \int d^3 f\left(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})\right)$$

different *f*, ex: PBE (physics), BLYP (chemistry)

$\rho(\vec{r})$ — LDA

$$E_{xc}[\rho] \approx E_{xc}^{LDA}[\rho] = \int e_{xc}^{hom}(\rho(\mathbf{r}))\, d^3 r$$

$$e_{xc}^{hom} = e_x^{hom} + e_c^{hom}$$

known QMC

Perdew's Jacob's Ladder