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TD 1: Hartree-Fock and Density-Functional Theory

We will apply Hartree-Fock and density-functional theories on a toy example of a ground-state calculation of the helium atom. We will consider an one-electron basis made of two *s*-type Gaussian functions centered on the nucleus, $\phi_s(\mathbf{r},\alpha) = (2\alpha/\pi)^{3/4} e^{-\alpha r^2}$, with the two exponents $\alpha_1 = 3.8$ and $\alpha_2 = 0.5$. Hartree atomic units are used everywhere.

1 Hartree-Fock

1.1 Hartree-Fock wave function and Hartree-Fock equations

1. Write down the Hartree-Fock (HF) ground-state wave function for He.
2. Recall the HF total energy expression and HF equations of an arbitrary closed-shell system in terms of spatial orbitals.
3. Derive the algebraic HF equations of an arbitrary closed-shell system in a basis (Roothaan equations).

1.2 Integrals over basis functions

1. Recall the general definition of the overlap, one-electron and two-electron integrals over basis functions and their symmetry properties with respect to permutation of the basis functions.
2. The expressions of the integrals over normalized s Gaussian basis functions (exponents α, β, γ and δ) for a single atom (with nuclear charge Z) are:
   - overlap integrals:
   $$(A|B) = \left(\frac{2\alpha}{\pi}\right)^{3/4}\left(\frac{2\beta}{\pi}\right)^{3/4}\left(\frac{\pi}{\alpha+\beta}\right)^{3/2}$$
   - kinetic integrals:
   $$(A|-\frac{1}{2}\nabla^2_{\mathbf{r}}|B) = \left(\frac{2\alpha}{\pi}\right)^{3/4}\left(\frac{2\beta}{\pi}\right)^{3/4}\frac{3\alpha\beta\pi^{3/2}}{(\alpha+\beta)^{5/2}}$$
   - nuclear-electron integrals:
   $$(A|-\frac{Z}{r}|B) = -\left(\frac{2\alpha}{\pi}\right)^{3/4}\left(\frac{2\beta}{\pi}\right)^{3/4}\frac{2\pi Z}{\alpha+\beta}$$
   - two-electron integrals (in chemist's notation):
   $$(AB|CD) = \left(\frac{2\alpha}{\pi}\right)^{3/4}\left(\frac{2\beta}{\pi}\right)^{3/4}\left(\frac{2\gamma}{\pi}\right)^{3/4}\left(\frac{2\delta}{\pi}\right)^{3/4}\frac{2\pi^{5/2}}{(\alpha+\beta)(\gamma+\delta)(\alpha+\beta+\gamma+\delta)^{1/2}}$$

   Calculate all the unique integrals for He for the two basis functions given previously.

1.3 Self-consistent-field iterations

1. Calculate the elements of the 2×2 core Hamiltonian matrix (i.e., the one-electron part of the Fock matrix). Obtain an initial guess for the orbital coefficients by solving the generalized eigenvalue equation with neglect of the two-electron part of the Fock matrix.
2. Calculate the elements of the 2×2 one-particle density matrix from the obtained occupied orbital coefficients, calculate the two-electron part of the 2×2 Fock matrix, and solve the generalized eigenvalue equation for the new orbital coefficients. Calculate the current value of the HF total energy.
3. Iterate step 2 until convergence. The coefficients of the occupied orbital should converge to $\mathbf{c}_1 = (0.300859, 0.811650)$.
4. Calculate the final HF total energy and its components (kinetic energy, nuclear-electron energy, and electron-electron energy). Check whether the virial theorem is satisfied. Comment.

2 Density-functional theory

2.1 Kohn-Sham equations

1. Write down the total energy of an arbitrary closed-shell system in density-functional theory (DFT) within the Kohn-Sham (KS) scheme in terms of spatial orbitals and the exchange-correlation density functional $E_{xc}[\rho]$. Compare to the HF energy expression.

2. Derive the KS equations of an arbitrary closed-shell system in terms of spatial orbitals. Explain how the exchange-correlation potential $v_{xc}(\mathbf{r})$ is obtained from the exchange-correlation functional $E_{xc}[\rho]$.

3. Write down the algebraic KS equations of an arbitrary closed-shell system in a basis. In comparison to HF, what additional quantities need to be calculated? How can the exchange-correlation potential contribution to the Fock matrix be evaluated in practice?

4. Write down the expression of the HF exchange potential. How does it compare with the KS exchange potential $v_x(\mathbf{r})$?

2.2 Approximate density functionals

1. We consider the following approximate local density functionals:
   - the Dirac (or Slater) exchange functional:

   $$E_x^{\mathrm{D}}[\rho] = C_x \int \rho(\mathbf{r})^{4/3} d\mathbf{r}$$

   with the constant $C_x = -(3/4)(3/\pi)^{1/3}$.

   - the Wigner correlation functional:

   $$E_c^{\mathrm{W}}[\rho] = \int \frac{a\rho(\mathbf{r})}{b + r_s(\mathbf{r})} d\mathbf{r}$$

   with the Wigner-Seitz radius $r_s(\mathbf{r}) = (3/(4\pi\rho(\mathbf{r}))^{1/3}$, and two constants $a = -0.29$ and $b = 5.1$. The Wigner functional was constructed from the low-density limit of the correlation energy of the uniform electron gas.

   Calculate the associated exchange and correlation potentials (by taking the functional derivatives) as a function of the density $\rho(\mathbf{r})$.

2. We perform a KS DFT calculation on the He atom (with the two basis functions given previously) using the standard local-density approximation (LDA) for the exchange-correlation functional: Dirac exchange functional + Vosko-Wilk-Nusair (VWN) correlation functional (obtained from a parametrization of the accurate correlation energy of the uniform electron gas). We obtain a total energy of $E_{\mathrm{LDA}} = -2.71592$ a.u.. The exchange and correlation energies are $E_x^{\mathrm{D}} = -0.866994$ a.u. and $E_c^{\mathrm{VWN}} = -0.112870$ a.u.. The coefficients of the occupied orbital are $\mathbf{c}_1 = (0.295500, 0.815618)$. Calculate the "exact" exchange energy (i.e., the HF exchange energy expression) with the LDA occupied orbital. Compare to the LDA exchange energy. The exact correlation energy is $E_c^{\mathrm{exact}} = -0.042$ a.u.. Comment on the accuracy of LDA.

3. We consider now generalized-gradient approximations (GGA) of the form

   $$E_{xc}^{\mathrm{GGA}}[\rho] = \int e_{xc}(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})) d\mathbf{r}$$

   where the energy density e_{xc} is a function of the density $\rho(\mathbf{r})$ and the gradient of the density $\nabla\rho(\mathbf{r})$.

   Give the general expression of the exchange-correlation potential for a GGA functional.

4. We perform a KS DFT calculation using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, which is a popular GGA functional. The total energy is $E_{\mathrm{PBE}} = -2.770319$ a.u., the exchange and correlation energies are $E_x^{\mathrm{PBE}} = -0.998401$ a.u. and $E_c^{\mathrm{PBE}} = -0.045508$ a.u.. Comment on the accuracy of PBE.