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http://www.physik.uni-regensburg.de/forschung/evers/courses/2021/comp_nanoscience.phtml

Computational Nanoscience: Exercise Sheet No. 6

Exercise 6.1: General questions on DFT

- Why did we introduce Kohn-Sham DFT? Is Kohn-Sham DFT formally exact? Is Kohn-Sham DFT also exact in practice when doing a calculation on a big molecule or a solid?
- Does full-CI in the complete-basis-set limit yield the same electron density as Kohn-Sham DFT with the exact exchange-correlation functional in the complete-basis-set limit?
- Does the Slater determinant Ψ_{KS} built of Kohn-Sham orbitals (computed from Kohn-Sham DFT with the exact exchange-correlation functional) yield the exact electron density from the equation

$$n(\mathbf{r}) = \langle \Psi_{\text{KS}} | \hat{n}(\mathbf{r}) | \Psi_{\text{KS}} \rangle ? \quad (1)$$

- Is the Kohn-Sham Slater determinant Ψ_{KS} equal to the many-electron ground state wavefunction?
- Employ Levy's search scheme to write Hartree-Fock as a density functional theory.

Exercise 6.2: Resolution of the identity for Kohn-Sham DFT

The resolution of the identity is a method to reformulate electronic-structure algorithms with the aim to accelerate the calculation. The underlying idea is the following: In four-center Coulomb integrals

$$(\mu\nu|\lambda\sigma) = \iint d^3\mathbf{r} d^3\mathbf{r}' \phi_\mu(\mathbf{r}) \phi_\nu(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_\lambda(\mathbf{r}') \phi_\sigma(\mathbf{r}'). \quad (2)$$

contain products of Gaussian basis functions $\phi_\mu(\mathbf{r}) \phi_\nu(\mathbf{r})$ and $\phi_\lambda(\mathbf{r}') \phi_\sigma(\mathbf{r}')$. These products are known and are approximated by a superposition

$$\phi_\mu(\mathbf{r}) \phi_\nu(\mathbf{r}) \approx \sum_P C_{\mu\nu}^P \varphi_P(\mathbf{r}). \quad (3)$$

where $\varphi_P(\mathbf{r})$ are Gaussian basis functions and called "RI basis functions". The number of RI basis functions is typically similar to the number of basis functions ϕ_ν for the Kohn-Sham orbitals. The superposition of Gaussians on the right-hand side of Eq. (3) gives an optimal approximation to the product $\phi_\mu(\mathbf{r}) \phi_\nu(\mathbf{r})$, if the coefficients $C_{\mu\nu}^P$ are chosen as

$$C_{\mu\nu}^P = \sum_Q (\mu\nu|Q) V_{PQ}^{-1} \quad (4)$$

where the three-center Coulomb integral $(\mu\nu|Q)$ and the Coulomb matrix V_{PQ} (note that V_{PQ}^{-1} is the PQ matrix element of the inverse Coulomb matrix) are given by

$$(\mu\nu|Q) = \iint d^3\mathbf{r} d^3\mathbf{r}' \phi_\mu(\mathbf{r}) \phi_\nu(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \varphi_Q(\mathbf{r}') \quad \text{and} \quad V_{PQ} = \iint d^3\mathbf{r} d^3\mathbf{r}' \varphi_P(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \varphi_Q(\mathbf{r}'). \quad (5)$$

- (a) Show that in the resolution-of-the-identity, four-center Coulomb integrals can be approximated as

$$(\mu\nu|\lambda\sigma) \approx (\mu\nu|\lambda\sigma)_{\text{RI}} = \sum_{PQ} (\mu\nu|P) V_{PQ}^{-1} (Q|\lambda\sigma). \quad (6)$$

- (b) In Kohn-Sham DFT calculations with a Gaussian basis, the matrix elements $V_{\mu\nu}^{\text{H}}$ of the Hartree potential are needed (as in the Hartree-Fock algorithm in Figure 5.2 in the lecture notes),

$$V_{\mu\nu}^{\text{H}} = 2 \sum_{\lambda\sigma} (\mu\nu|\lambda\sigma) D_{\lambda\sigma} \quad \text{with} \quad D_{\lambda\sigma} = \sum_{m=1}^{N/2} C_{m\lambda} C_{m\sigma}. \quad (7)$$

Suppose, we have a small molecule, so all Gaussian basis functions are considerably overlapping with each other such that Eq. (7) is scaling as $O(N_{\text{atom}}^4 N_{\text{SCF}})$. Note that the density matrix \mathbf{D} changes in every SCF step, such that Eq. (7) needs to be repeated in every SCF step (N_{SCF} : total number of SCF steps). How can one reduce the computational cost of Eq. (7) using the resolution-of-the-identity from Eq. (6)?

- (c) At the beginning of a Hartree-Fock calculation, one computes the 4c-integrals $(\mu\nu|\lambda\sigma)$ that needs considerable amount of time. In DFT with the RI approximation, we only need to compute three-center Coulomb integrals $(\mu\nu|Q)$ and the Coulomb matrix V_{PQ} . Why is the computation of $(\mu\nu|Q)$ and V_{PQ} much faster than the computation of $(\mu\nu|\lambda\sigma)$?
- (d) Now, we test the computational cost of Kohn-Sham DFT without RI and with RI for the H_2 chains as on Exercise Sheet 4, exercise 4.1 (g). For benchmarking the computational time of DFT and RI-DFT, use a def2-QZVPP basis set and the PBE functional. You find a video on DFT calculations with Turbomole with the title “8.6 Kohn-Sham DFT in Turbomole (08.06.2020)”. Please fill in the following table:

N_{H_2}	CPU time of HF (s)	CPU time of DFT (dscf) (s)	CPU time of RI-DFT (ridft) (s)
1	1.06		
2	8.7		
4	46		
8	231		

Note that applying RI to the exchange matrix in Hartree-Fock does not yield considerable speedups because of algebraic structure of the exchange, details e.g. in F. Weigend, A fully direct RI-HF algorithm: Implementation, optimised auxiliary basis sets, demonstration of accuracy and efficiency, *Phys. Chem. Chem. Phys.* **4**, 4285-4291 (2002).

- (e) Assume the CPU time scales as

$$\text{CPU time} = C \cdot N_{\text{H}_2}^\alpha.$$

Determine the exponent α for DFT and RI-DFT when using your data points (1) 1 H_2 and 2 H_2 and (2) 4 H_2 and 8 H_2 .

- (f) Briefly interpret the timings and the exponents you obtained.