DFT meets OT

Worksheet 1 (January 17, 2018)

Problem 1

Consider the antisymmetrized product wave function Ψ given in the lecture,

$$\Psi(\mathbf{x}_1, ..., \mathbf{x}_N) \;=\; \frac{1}{\sqrt{N!}} \sum_{\wp \in S_N} \operatorname{sign}(\wp) \prod_{k=1}^{N} \psi_{\wp(k)}(\mathbf{x}_k) \qquad \Big(\mathbf{x}_k = (\mathbf{r}_k, \sigma_k)\Big), \tag{1}$$

where $\psi_1(\mathbf{x}) = \phi_1(\mathbf{r})\alpha(\sigma)$, $\psi_2(\mathbf{x}) = \phi_1(\mathbf{r})\beta(\sigma)$, $\psi_3(\mathbf{x}) = \phi_2(\mathbf{r})\alpha(\sigma)$, etc.,

$$\alpha(\uparrow) = 1, \quad \alpha(\downarrow) = 0 \qquad (\text{"spin up"}), \tag{2}$$

$$\beta(\uparrow) = 0, \quad \beta(\downarrow) = 1 \qquad (\text{"spin down"}), \tag{3}$$

and the $\phi_n(\mathbf{r})$ are the solutions of the **one-particle** Schrödinger equation

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + v(\mathbf{r}) \right\} \phi_n(\mathbf{r}) \;=\; \epsilon_n \, \phi_n(\mathbf{r}) \qquad \Big(\epsilon_1 \le \epsilon_2 \le \epsilon_3 \le ...\Big). \tag{4}$$

(a) Show that Ψ is an eigenfunction of the non-interacting N-electron Hamiltonian

$$\hat{H}_N^{(0)}[v] \;=\; \sum_{i=1}^{N} \left\{ -\frac{\hbar^2}{2m} \nabla_i^2 + v(\mathbf{r}_i) \right\} \;\equiv\; \sum_{i=1}^{N} \hat{h}_i \tag{5}$$

to the eigenvalue $E = 2\sum_{n=1}^{N/2} \epsilon_n$.

(b) Show that Ψ (for even $N \in \{2, 4, 6, ...\}$) has the electron density

$$\rho(\mathbf{r}) \;=\; 2 \sum_{n=1}^{N/2} |\phi_n(\mathbf{r})|^2. \tag{6}$$

Hint 1: For $\mathbf{x} = (\mathbf{r}, \sigma)$, use the notation $\sum_{\sigma \in \{\uparrow,\downarrow\}} \int \mathrm{d}^3r \, f(\mathbf{r}, \sigma) \equiv \int \mathrm{d}^3x \, f(\mathbf{x})$.
Hint 2: The single-particle wave functions $\psi_k(\mathbf{x})$ are pairwise orthonormal,

$$\int \mathrm{d}^3x \, \psi_k^*(\mathbf{x}) \, \psi_{k'}(\mathbf{x}) \;=\; \delta_{k,k'} \qquad (k, k' \in \{1, ..., N\}). \tag{7}$$

Problem 2

Let $\Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2)$ be a (correctly antisymmetric) wave function for $N = 2$ electrons.

(a) Which ones of the following terms can be evaluated without knowing Ψ explicitly?

$$\big|\Psi(\mathbf{r}\uparrow, \mathbf{r}\downarrow)\big|^2, \qquad \big|\Psi(\mathbf{r}\uparrow, \mathbf{r}\uparrow)\big|^2, \qquad \sum_{\sigma_1,\sigma_2} \big|\Psi(\mathbf{r}\sigma_1, \mathbf{r}\sigma_2)\big|^2. \tag{8}$$

As a region $\Omega = \Omega_R(\mathbf{r}_0)$ in space, we consider a ball with radius R centered at $\mathbf{r} = \mathbf{r}_0$,

$$\Omega_R(\mathbf{r}_0) \;=\; \Big\{\mathbf{r} \in \mathbb{R}^3 \;\Big|\; |\mathbf{r} - \mathbf{r}_0| \leq R\Big\}. \tag{9}$$

(b) Give a probability interpretation for the number

$$P_R(\mathbf{a}, \mathbf{b}; \sigma_1, \sigma_2) \;=\; \int_{\Omega_R(\mathbf{a})} \mathrm{d}^3 r_1 \int_{\Omega_R(\mathbf{b})} \mathrm{d}^3 r_2 \left| \Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2)\right|^2 \tag{10}$$

in the two cases (i) $\Omega_R(\mathbf{a}) \cap \Omega_R(\mathbf{b}) = \emptyset$, (ii) $\mathbf{a} = \mathbf{b}$.

(c) Provided that $\Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2)$ is a continuous function of both $\mathbf{r}_1 \in \mathbb{R}^3$ and $\mathbf{r}_2 \in \mathbb{R}^3$, determine the limit

$$p(\mathbf{a}, \mathbf{b}; \sigma_1, \sigma_2) \;=\; \lim_{R\to 0} \frac{P_R(\mathbf{a}, \mathbf{b}; \sigma_1, \sigma_2)}{(\frac{4\pi}{3}R^3)^2}. \tag{11}$$

(d) What can you tell about the quantities

$$p(\mathbf{a}, \mathbf{a}; \uparrow, \uparrow), \qquad p(\mathbf{a}, \mathbf{a}; \uparrow, \downarrow). \tag{12}$$

What is the probability (density) for finding the two electrons on top of each other?

Problem 3

The most general form of a wave function for $N = 2$ electrons is

$$\begin{aligned}\Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2) \;=\; & \psi_1(\mathbf{r}_1, \mathbf{r}_2)\alpha(\sigma_1)\alpha(\sigma_2) \;+\; \psi_2(\mathbf{r}_1, \mathbf{r}_2)\alpha(\sigma_1)\beta(\sigma_2) \\ & +\; \psi_3(\mathbf{r}_1, \mathbf{r}_2)\beta(\sigma_1)\alpha(\sigma_2) \;+\; \psi_4(\mathbf{r}_1, \mathbf{r}_2)\beta(\sigma_1)\beta(\sigma_2),\end{aligned}$$

with the spin functions $\alpha(\sigma)$ and $\beta(\sigma)$ from Eqs. (2) and (3).

(a) Using the short-hand notations $\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(1, 2)$ and $\chi(\sigma_1, \sigma_2) = \chi(1, 2)$, find the conditions on the functions $\psi_k(\mathbf{r}_1, \mathbf{r}_2)$ ($k = 1, 2, 3, 4$) that make Ψ antisymmetric.

(b) For non-interacting electrons, we expect the product form

$$\psi_k(\mathbf{r}_1, \mathbf{r}_2) \;=\; A_k\, \phi_1(\mathbf{r}_1)\, \phi_2(\mathbf{r}_2) \;+\; B_k\, \phi_2(\mathbf{r}_1)\, \phi_1(\mathbf{r}_2), \tag{13}$$

with $\int \mathrm{d}^3 r\, |\phi_1(\mathbf{r})|^2 = \int \mathrm{d}^3 r\, |\phi_2(\mathbf{r})|^2 = 1$.
What can you tell about the values of the coefficients A_k, B_k in the following cases?

(i) $\phi_1(\mathbf{r}) = \phi_2(\mathbf{r}) \equiv \phi(\mathbf{r})$.

(ii) $\int \mathrm{d}^3 r\, \phi_1^*(\mathbf{r})\, \phi_2(\mathbf{r}) = 0$.

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Worksheet 2 (January 29, 2018)

Problem 1

(a) Show that the function $v : \mathbb{R}^3 \backslash \{0\} \to \mathbb{R}, v(\mathbf{r}) = -\frac{1}{|\mathbf{r}|}$ belongs to $L^{3/2}(\mathbb{R}^3) \oplus L^\infty(\mathbb{R}^3)$.

(b) Consider the energy function for the Hydrogen atom ($N = 1$).

$$E[\psi] = \sum_{s \in \mathbb{Z}_2} \int_{\mathbb{R}^3} |\nabla \psi(\mathbf{r}, s)|^2 - \frac{1}{|\mathbf{r}|} |\psi(\mathbf{r}, s)|^2 d\mathbf{r}.$$

Show that the above energy is not well-defined in $L^2(\mathbb{R}^3 \times \mathbb{Z}_2)$.
(Hint: Consider the function $\psi(r, s) = \sqrt{(2\pi)}\delta_{1/2}(s)e^{-|r|}/|r|$.
Show that $\psi \in L^2(\mathbb{R}^3 \times \mathbb{Z}_2)$ with $\|\psi\|_{L^2} = 1$, but not in $H^1(\mathbb{R}^3 \times \mathbb{Z}_2)$. Conclude by comparing with the right-hand term.)

Problem 2

Consider $\rho : \mathbb{R}^3 \to \mathbb{R}$ a probability density and a (admissible) function $\psi \in H^1((\mathbb{R}^3 \times \mathbb{Z}_2)^N)$ such that $\|\psi\|_{L^2} = 1, \psi \mapsto \rho$ and ψ is anti-symmetric.

(a) Show that

$$\int_{\mathbb{R}^{3N}} \sum_{i=1}^{N} v(\mathbf{r}_i)\rho^\psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) d\mathbf{r}_1 \ldots d\mathbf{r}_N = N \int_{\mathbb{R}^3} v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r},$$

where $\rho^\psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_{s_1,\ldots,s_N \in \mathbb{Z}_2} |\psi(\mathbf{r}_1, s_1, \ldots, \mathbf{r}_N, s_N)|^2$.

(b) Denote by $A[\rho] = \int_{\mathbb{R}^3} v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$. Consider $\rho_\epsilon(\mathbf{r}) = \rho(\mathbf{r}) + \epsilon\xi(\mathbf{r})$ with $\xi(\mathbf{r}) \geq 0$ and $\int_{\mathbb{R}^3} \xi(\mathbf{r})d\mathbf{r} = 0$. Compute the limit

$$\lim_{\epsilon \to 0} \frac{A[\rho_\epsilon] - A[\rho]}{\epsilon}.$$

(c) Show that $\rho \geq 0$, $\|\rho\|_{L^1} = 1$ and $\sqrt{\rho} \in H^1(\mathbb{R}^3)$.
(Hint: Use Cauchy-Schwarz and notice that $|\nabla\sqrt{g}|^2 = \frac{|\nabla g|^2}{g}$.)

Problem 3

(a) Consider the Lorenzian density $\rho : \mathbb{R} \to \mathbb{R}$, $\rho(r) = \frac{1}{\pi(1+r^2)}$ and the associate co-motion function $f(r) = -1/r$. Show that the SCE-ansatz $\gamma_f(r_1, r_2) = \delta(r_2 - f(r_1))\rho(r_1)$ (or, equivalently, $\gamma_f = (Id, f)_\sharp \rho$) is not in $H^1(\mathbb{R}^2, \mathbb{R})$.
(Hint: Draw the graph $\{(r, f(r)) \in \mathbb{R}^2 : r \in \mathbb{R}\backslash\{0\}\}$. Write the definition of the gradient of γ at a point $(r, f(r))$).

Problem 4

(a) Give an example of a function $g : \mathbb{R} \to \mathbb{R}$ that is lower-semi continuous but not continuous. Justify your example.

(b) Suppose X is a metric space (if you prefer you can assume $X = \mathbb{R}^d$). If $g : X \to \mathbb{R} \cup \{+\infty\}$ is lower semi-continuous and X is compact, then there exists $\bar{x} \in X$ such that $g(\bar{x}) = \min\{g(x) : x \in X\}$.