Introduction to electronic structure theory: Assignment 1

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Recommend to submit the homework typed using LaTeX.

1. Consider a system of two spin 1/2 particles in the singlet state

$$|\psi_S\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle).$$

   Let $\mathbf{s}_i$ be the spin operator corresponding to spin i $(i = 1, 2)$, and $\mathbf{a}, \mathbf{b} \in \mathbb{R}^3$ be 2 arbitrary directions. Show that

$$\langle\psi_S|(\mathbf{a}\cdot\mathbf{s}_1)(\mathbf{b}\cdot\mathbf{s}_2)|\psi_S\rangle = -(\mathbf{a}\cdot\mathbf{b})\,(\hbar/2)^2\,.$$

   (Hint: use tensor product Hilbert space.)

2. Let

$$H = \frac{p^2}{2m} + V(x).$$

   $V(x)$ is bounded and is sufficiently smooth. Prove that Ehrenfest's theorem formally holds for any initial state, i.e.

$$\frac{d\langle x\rangle}{dt} = \frac{1}{m}\langle p\rangle\,,$$
$$\frac{d\langle p\rangle}{dt} = -\left\langle\frac{dV}{dx}\right\rangle.$$

   (Remark: Note the connection to Newton's law in classical physics.)

   (Hint: use commutation relation)

3. **Project (optional):** a) The Hamiltonian for 1D hydrogen atom with soft Coulomb potential is given as follows

$$H = -\frac{1}{2}\frac{d^2}{dx^2} + V_I(x).$$

Compare with the 3D hydrogen atom, the electron-ion interaction is replaced by the following potential

$$V_I(x) = \int v_c(x, y)m(y)dy.$$

Here the Coulomb interaction is replaced by the soft Coulomb interaction

$$v_c(x) = \frac{1}{\sqrt{x^2 + 1}},$$

and the ionic charge is replaced by the pseudocharge

$$m(x) = -\frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}}$$

with $\sigma = 0.1$.

Numerically solve the eigenvalue problem using finite difference discretization with Dirichlet boundary condition. Compute the ground state energy of the 1D hydrogen atom (with at least 3 digit accuracy), denoted by E_0, and plot the shape of the ground state wavefunction ψ_0.

b) Use the tools built in a) and solve the ground state energy of H_2^+ molecule. The Hamiltonian is

$$H = -\frac{1}{2}\frac{d^2}{dx^2} + V(x),$$

where

$$V(x) = V_I(x) + V_I(x - R),$$

and $R > 0$ is the distance between two hydrogen atoms.

Compute the ground state energy $E(R)$ of H_2^+ as a function of the interatomic distance R. Plot the shape of the ground state wavefunction when $R = 5$. Compare the ground state energy $E(R)$ with $2E_0$ when R becomes sufficiently large.