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Problem 8.1: Variational ansatz for the hydrogen atom

[**Oral** | 6 (+2 bonus) pt(s)]

ID: `ex_hydrogen_atom_variational:`

Learning objective

We illustrate the principles of variational methods through two fundamental quantum systems: first by exploring key aspects of the formalism using the one-dimensional harmonic oscillator, and then by implementing an effective ansatz for the hydrogen atom ground state.

a) (i) Show that in 1D the kinetic energy contribution should be calculated as **4**pt(s)

$$-\left\langle \psi \left| \frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right| \psi \right\rangle = \frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} \left| \frac{d\psi(x)}{dx} \right|^2 dx. \tag{1}$$

Hint: Integrate $|\frac{d\psi(x)}{dx}|^2$ by parts.

(ii) Explain why you can have problems if you actually use

$$-\left\langle \psi \left| \frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right| \psi \right\rangle = -\frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} \psi^*(x) \frac{d^2\psi(x)}{dx^2} dx, \tag{2}$$

instead of equation (1). For example, consider the problem of a one-dimensional harmonic oscillator with an ansatz of the form

$$\psi_0(x, \alpha) = Ae^{-\alpha|x|}, \tag{3}$$

where A is a normalization constant and α a real positive number.

Show that equations (1) and (2) give rise to contradictory results and explain why using eq. (1) is the correct approach.

*b) Show that in three-dimensions the analog of (1) is given by **+2**pt(s)

$$-\left\langle \psi \left| \frac{\hbar^2}{2m} \nabla^2 \right| \psi \right\rangle = \frac{\hbar^2}{2m} \int (\boldsymbol{\nabla}\psi^*(r)) \cdot (\boldsymbol{\nabla}\psi(r)) d^3r. \tag{4}$$

Hint: Follow the same idea in (i) and use Gauss's theorem.

Now we focus once again on the hydrogen atom problem. Consider the ansatz

$$\psi(r, \theta, \phi) = e^{-r/\alpha}, \tag{5}$$

where α is a scale parameter and there is no angular dependence of $\psi(r)$ since the ground state function is spherically symmetric. This ansatz has no nodes and it also vanishes at infinity.

c) Use the variational method to estimate the ground state energy of the hydrogen atom with this ansatz. Observe that here you should use equation (4) for the kinetic term contribution. **2**$^{\text{pt(s)}}$

Problem 8.2: Four level system degenerate perturbation theory [**Written** | 4 pt(s)]

`ID: ex_degenerate_pt_4level_system:`

Learning objective

Within a four level-system scenario, we will use degenerate perturbation theory to obtain the corrections to the eigenenergies of the Hamiltonian under the influence of a perturbation. As we will see, in some cases first-oder perturbation theory is already enough to capture the exact eigenvalues of a physical system.

Consider a generic four level system with an unperturbed Hamiltonian $\hat{H}_0$ given by

$$\hat{H}_0 = E_0 \begin{pmatrix} 15 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 \\ 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 3 \end{pmatrix} \tag{6}$$

which is subject to a perturbation $\hat{H}_1$ given by

$$\hat{H}_1 = \frac{E_0}{100} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \tag{7}$$

a) Find the eigenstates of the unperturbed Hamiltonian $\hat{H}_0$ as well as the exact eigenvalues of the total Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_1$. **2**$^{\text{pt(s)}}$

b) Find the eigenenergies of $\hat{H}$ to first and second order perturbation order. How do they compare with the exact values obtained in (a)? **2**$^{\text{pt(s)}}$

Problem 8.3: Perturbing the one-dimensional harmonic oscillator [**Oral** | 2 pt(s)]

`ID: ex_time_dep_pt_1d_harmonic_osc:`

Learning objective

This exercise exemplifies time-dependent perturbation theory for the canonical example of a one-dimensional harmonic oscillator under the influence of a constant perturbing potential during a certain time interval.

A particle of mass m is in the ground state of a one-dimensional harmonic oscillator potential. The oscillator frequency is ω. At $t = 0$, a weak constant force $\mathcal{F}$ is applied and acts until time $t = \tau$ such that the perturbing potential is given by

$$\hat{W}(x, t) = -\mathcal{F}x, 0 < t < \tau. \tag{8}$$

Use first-order time-dependent perturbation theory to find the value (or values) of τ, call them τ_{max}, that maximize the probability of a transition to the first excited state ($n = 1$).