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Problem 7.1: Variational ansatz for the hydrogen atom   [**Oral** | 6 (+2 bonus) pt(s)]

ID: ex_hydrogen_atom_variational:aqt2324

> **Learning objective**
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> In order to illustrate how variational methods work, we are going to explore a few considerations regarding the formalism in the context of a one-dimensional harmonic oscillator, and also apply a particularly good ansatz to describe the ground state of the hydrogen atom.

a) (i) Show that in 1D the kinetic energy contribution should be calculated as   **4**$^{\text{pt(s)}}$

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

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

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

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

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. (2) is the correct approach.

*b) Show that in three-dimensions the analog of (1) is given by   **+2**$^{\text{pt(s)}}$

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

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 **2**pt(s) ansatz. Observe that here you should use equation (4) for the kinetic term contribution.

Problem 7.2: The Stark Effect   [**Oral** | 4 pt(s)]

ID: ex_stark_effect_nondegenerate_pt:aqt2324

Learning objective

In this task, we will see the effect of an electric field on the ground state of the hydrogen atom and explore its polarizability using nondegenerate perturbation theory.

The effect that an external electric field has on the energy levels of an atom is called the Stark effect. In the absence of an electric field, the (unperturbed) Hamiltonian of the hydrogen atom (in CGS units) is:

$$\hat{H}_0 = \frac{\hat{\boldsymbol{p}}^2}{2\mu} - \frac{e^2}{r}.$$

The eigenfunctions of this Hamiltonian, $\psi_{nlm}(\boldsymbol{r})$, are given by

$$\langle r\theta\varphi \mid nlm \rangle = \psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm}(\theta, \varphi).$$

a) Consider an external uniform weak electric field, which is directed along the positive z-axis, **2**pt(s) $\overrightarrow{\mathcal{E}} = \mathcal{E}\boldsymbol{k}$, on the ground state of a hydrogen atom. Ignoring the spin degrees of freedom, calculate the energy using second-order perturbation theory.

b) Find an approximate value for the polarizability of the hydrogen atom. **2**pt(s) [**Hint**: Use $\langle 100|\hat{Z}|100 \rangle = 0$ and that the set of states $|nlm\rangle$ is complete].

Problem 7.3: The Stark Effect revisited   [**Written** | 4 pt(s)]

ID: ex_stark_effect_degenerate_pt:aqt2324

Learning objective

In this task, we will see the effect of an uniform weak electric field on the excited states of the hydrogen atom using degenerate perturbation theory.

When the external electric field is turned on, some energy levels will split. The energy due to the interaction between the dipole moment of the electron ($\boldsymbol{d} = -e\boldsymbol{r}$) and the external electric field ($\overrightarrow{\mathcal{E}} = \mathcal{E}\boldsymbol{k}$) is given by

$$\hat{H}_p = -\boldsymbol{d} \cdot \overrightarrow{\mathcal{E}} = e\boldsymbol{r} \cdot \overrightarrow{\mathcal{E}} = e\mathcal{E}\hat{Z}$$

In the absence of any external electric field, the first excited state (i.e., $n = 2$) is fourfold degenerate: the states $|nlm\rangle = |200\rangle, |210\rangle, |211\rangle$, and $|21-1\rangle$ have the same energy $E_2 = -R_y/4$, where $R_y = \mu e^4 / (2\hbar^2) = 13.6\text{eV}$ is the Rydberg constant.

a) In order to calculate the energy levels of the $n = 2$ states, first determine the matrix elements of **2**pt(s) the 4×4 Hamiltonian $\hat{H}_p$.

b) Diagonalize the matrix obtained above and determine the eigenenergies of $n = 2$ states up to (first order). Are all the degeneracies lifted?

2pt(s)