Problem Set IV: CHEM321: Physical Chemistry II[*]

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1. [40 points] **Proof of the variational principle**

Postulate VI reads, "The set of eigenfunctions for a physical observable form a complete set." This means we can write any other function as a linear combination of eigenfunctions of some operator. We can use this fact to prove the variational principle.

$\hat{\mathcal{H}}\psi_n = E_n\psi_n$ and we are looking for the ground state solution, ψ_0, with energy E_0. We can write the trial wavefunction, ϕ, as a linear combination of ψ_n's (never mind we don't know what ψ_0 is, let alone all of the other ψ_n's):

$$\phi = \sum_n c_n \psi_n \tag{1}$$

where c_n are the coefficients of the linear combination.

A consequence of the eigenfunctions being a complete set is that the are orthogonal to each other. As a rule, we tend to normalize them also, making the ψ_n **orthonormal** (i.e., **ortho**gonal and **normal**ized):

$$\int \psi_i^* \psi_j \, \mathrm{d}\tau = \delta_{ij} \tag{2}$$

(a) [15 points] Show that:

$$c_n = \int \psi_n^* \phi \, \mathrm{d}\tau \tag{3}$$

Since we do not know the ψ_n from which we are constructing ϕ, Eq. 1 is known as a *formal expansion*. Substituting this formal expansion into the definition of E_ϕ gives:

$$E_\phi = \frac{\int \phi^* \hat{\mathcal{H}} \phi \, \mathrm{d}\tau}{\int \phi^* \phi \, \mathrm{d}\tau} \tag{4}$$

$$E_\phi = \frac{\sum_n c_n^* c_n E_n}{\sum_n c_n^* c_n} \tag{5}$$

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[*] Adapted from McQuarie and Simon, *Physical Chemistry: A Molecular Approach*

(b) [10 points] Show that substituting Eq. 1 into Eq. 4 yields Eq. 5

(c) [15 points] Add and subtract E_0, the ground state energy (i.e., lowest energy), from each term to give:

$$\begin{aligned} E_\phi &= E_0 + \frac{\sum_n c_n^* c_n (E_n - E_0)}{\sum_n c_n^* c_n} && (6) \\ E_\phi - E_0 &= \frac{\sum_n c_n^* c_n (E_n - E_0)}{\sum_n c_n^* c_n} && (7) \end{aligned}$$

Prove that every term on the right-hand-side of Eq. 7 is positive, and therefore $E_\phi \geq E_0$.

2. [30 points] A three-dimensional, spherically symmetric, isotropic harmonic oscillator experiences a potential, $V(r) = \frac{1}{2}kr^2$. The Hamiltonian operator for this system is:

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2\mu r^2} \frac{\mathrm{d}}{\mathrm{d}r}\left(r^2 \frac{\mathrm{d}}{\mathrm{d}r}\right) + \frac{1}{2}kr^2 \tag{8}$$

Physically this system is kind of like a particle of mass μ on a spring with force constant k with one end fixed at the origin, but free to rotate...

(a) [10 points] Apply the variational principle to this system, with $\phi = \mathrm{e}^{-\alpha r^2}$ and α as your variational parameter to estimate the ground state energy of this system.

(b) [10 points] Apply the variational principle to this system, with $\phi = \mathrm{e}^{-\alpha r}$ and α as your variational parameter to estimate the ground state energy of this system.

(c) [10 points] $E_0^{\text{exact}} = \frac{3}{2}h\nu$. Which ϕ gave you a better estimate of E_0^{exact}. Why?

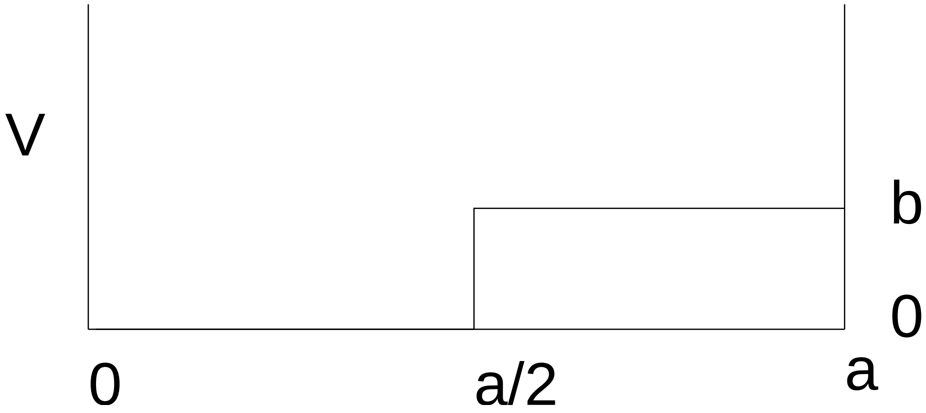
3. [30 points] For each system below, identify $\hat{\mathcal{H}}^{(0)}$, $\hat{\mathcal{H}}^{(1)}$, $\psi^{(0)}$, and $E^{(0)}$, and then use perturbation theory to calculate the first order correction to the ground state energy. 5 points for identification, 5 points for the first order correction, for each system.

(a) A one-dimensional anharmonic oscillator with

$$V(x) = \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 + \frac{1}{24}\beta x^4 \tag{9}$$

(b) A one-dimensional particle in a stepped box.

$$\begin{aligned} V(x) &= 0 \quad 0 < x < \frac{a}{2} \\ V(x) &= b \quad \frac{a}{2} < x < a \\ V(x) &= \infty \quad x < 0, x > a \end{aligned}$$



(c) A hydrogen atom in an electric field of strength, $\mathcal{E}$

$$\hat{\mathcal{H}} = -\frac{\hbar}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} + e\mathcal{E}r\cos\theta \tag{10}$$