Problem Set 1

CHEM 26800/36800 and MENG 25510/35510

Due March 28, 2024

1. Consider some normalized trial wave function $|\Psi\rangle$ that is orthogonal to the subspace spanned by the lowest n energy eigenstates. Show that

$$\mathcal{E}_{n+1} \leq \langle\Psi|\hat{H}|\Psi\rangle$$

where $\mathcal{E}_{n+1}$ is the energy of the $n+1$ eigenstate.

2. Assume we are only using real wave functions and consider the functional

$$F[\Psi] = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

This functional is stationary at the energy eigenstates. Here we will do a simple computation that confirms this for a special case. Take $|\Psi\rangle$ to be

$$|\Psi\rangle = |\Phi_1\rangle + \sum_{\alpha} \varepsilon_\alpha |\Phi_\alpha\rangle$$

where each ε_α is small. This is equivalent to the first excited state perturbed by some small amount in all other energy eigenstates. Evaluate $F[\Psi]$ including only terms quadratic in ε. Show that all linear terms of ε cancel and explain why this means the function is indeed stationary at $|\Phi_1\rangle$. Do any ε drop out to quadratic order? Discuss the nature of this critical point.

3. Consider a particle in a potential $V(x) = \lambda x^4$ so that the Hamiltonian is of the form

$$H(x) = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \lambda x^4$$

Here, λ is some real-valued constant. Consider a Gaussian trial wave function with a parameter α as

$$\xi(x, \alpha) = e^{-\alpha x^2/2}$$

Find the variationally optimized wave function $\xi(x, \alpha_0)$ and its corresponding energy.

4. Consider the azomethane molecule which has a chemical formula of $C_2N_2H_6$ and the 6-31G basis set. How many basis functions would we have in a calculation of azomethane?

5. Three spin 1/2 particles have spins $\hat{\mathbf{S}}_1$, $\hat{\mathbf{S}}_2$, $\hat{\mathbf{S}}_3$. What are the possible eigenvalues of $\hat{\mathbf{S}}^2$ where $\hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_3$? What are the multiplicities of each eigenvalue?