Quantum Chemistry Problem Set 4

Problem 1: Prove the following relationships for the harmonic oscillator creation/annihilation operators. (Here H is the harmonic osc. hamiltonian).

1. $[n, a] = -a$
2. $[n, a^\dagger] = a^\dagger$
3. $$|\phi_n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}|\phi_o\rangle$$
4. $$\langle\phi_n|x|\phi_m\rangle = \sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n+1}\delta_{m,n+1} + \sqrt{n}\delta_{m,n-1}\right)$$
5. Virial Relation: $$\langle\phi_n|T|\phi_n\rangle = \langle\phi_n|V|\phi_n\rangle$$
6. $$-\frac{i}{\hbar}[H, x^2]$$
7. $$-\frac{i}{\hbar}[H, px + xp]$$

Problem 2. Using Mathematica, make plots of the first 5 Harmonic Oscillator eigenfunctions for the case of $m\omega/\hbar = 1$. (Use the HermiteH[] function.)

Problem 3. One of the parallels between quantum mechanics and classical mechanics can be drawn using the Heisenberg representation which focuses upon the time evolution of operators and expectation values rather than wavefunctions. The Heisenberg equations of motion for a quantum operator is similar to the classical equations of motion except that the commutation bracket is used rather than the Poisson bracket. I.e

$$i\hbar\frac{\partial O}{\partial t} = [H, O]$$

In a similar sense, the equation of motion for expectation values of operators can be computed as

$$i\hbar\frac{\partial\langle O\rangle}{\partial t} = \langle[H, O]\rangle$$

Derive the Heisenberg equations of motion for n, x, and p for a particle in a Harmonic well. Compare to their classical analogs.

Problem 4. Consider a particle in Morse oscillator well with

$$V(x) = D_e(1 - e^{ax})^2 - D_e.$$

1. Expand this potential about its minimum at $x = 0$ up to 3^{rd} order in x. From the second-derivative term, derive an expression for the Harmonic oscillator frequency for a particle of mass m in this well.

2. Now, using the corresponding creation/annihilation operators and your series above, write the potential in terms of the creation/annihilation operators including up to tri-linear terms (i.e. terms like aaa and $a^\dagger aa$, etc...

3. Estimate the ground state energy for this system by taking the expectation value

$$\langle E \rangle = \langle \phi_o | \frac{p^2}{2m} + V | \phi_o \rangle$$

using your approximate form of V (note...factor out a harmonic oscillator part and an anharmonic correction term). Do any of your tri-linear terms contribute?

Problem 5. Consider a particle in a ramp potential $V = bx$ for $x > 0$ and $V = \infty$ for $x \le 0$ (sketched below). Using $\psi(x) = xExp[-ax^2]$ as a un-normalized trial function and a as a variational parameter, estimate the ground-state energy. Letting $b = 0.1$, $m = 1$ and $\hbar = 1$, plot $\langle E \rangle$ vs a and show that your variational energy converges towards the true energy from above. Note, you will need to limit the range of your integration to $[0, \infty)$ in computing integrals.