PROBLEM SET SOLUTIONS

CHAPTER 9, Levine, *Quantum Chemistry,* 5th Ed.

9.1 For the anharmonic oscillator with the Hamiltonian

$$H = -\underline{h}^2/(2m)\ \{d^2/dx^2\} + k\ x^2/2 + c\ x^3 + d\ x^4$$

evaluate E^1 for the first excited state, taking the unperturbed system as the harmonic oscillator.

HINT: Example p.248 (5th Ed.) shows how to calculate E^1 for the ground state of the harmonic oscillator. Use the same method, just change the wavefunction to that for the first excited state.

$E_N{}^1 = H_{NN}{}^1 = \int (\psi_N{}^0)^* H^1\ \psi_N{}^0 d\tau$, N = 1 for first excited state

$H^1 = H - H^0$

$H^0 = -\underline{h}^2/(2m)\ \{d^2/dx^2\} + k\ x^2/2$

$H^1 = c\ x^3 + d\ x^4$

For the harmonic oscillator, $\alpha = 2\pi\nu m/\underline{h} = 4\pi^2\nu m/h$ &

v = 0 is the ground state: $\psi_0 = c_0\ e^{-\alpha x**2/2}$, $c_0 = (\alpha/\pi)^{1/4}$

Example p. 248 shows that the first order correction to the ground state energy of the anharmonic oscillator is

$$E_0^1 = H_{00}^1 = 3d/(4\alpha^2) = 3dh^2/[64\pi^4\nu^2m^2]$$

For the harmonic oscillator

v = 1 is the first excited state: $\psi_1 = c_1 x\ e^{-\alpha x^{**}2/2}$, $c_1 = (4\alpha^3/\pi)^{1/4}$

The first order correction to the energy of the first excited state of the anharmonic oscillator is

$$E_1^1 = H_{11}^1 = \int (\psi_1^0)^* H^1\ \psi_1^0 d\tau$$

$$= \int_{-\infty}^{\infty} (c_1 x\ e^{-\alpha x^{**}2/2})^2\ (cx^3 + dx^4)dx$$

$$= (c_1)^2 \int_{-\infty}^{\infty} x^2\ e^{-\alpha x^{**}2}(cx^3 + dx^4)dx$$

$$= c\ (c_1)^2 \int_{-\infty}^{\infty} x^5\ e^{-\alpha x^{**}2}\ dx + d\ (c_1)^2 \int_{-\infty}^{\infty} x^6\ e^{-\alpha x^{**}2}\ dx$$

first term is even x odd, so integral = 0

$$E_1^1 = 2d\ (c_1)^2 \int_0^{\infty} x^6\ e^{-\alpha x^{**}2}\ dx$$

$$= 2d\ (c_1)^2\ (15/2^4)(\pi/\alpha^7)^{1/2}$$

$$= 2d\,(4\alpha^3/\pi)^{1/2}(15/2^4)(\pi/\alpha^7)^{1/2}$$

$$= d15/(4\alpha^2)$$

$$= d15/[4(4\pi^2\nu m/h)^{\,2}]$$

$$= d15h^2/[64\pi^4\nu^2m^2]$$