Quantum Chemistry

Corrections 7A

1. Identify $\hat{H}^{(0)}, \hat{H}^{(1)}, \psi^{(0)}$ *and* $E^{(0)}$ *for the following problems*

a. An oscillator governed by the potential

$$U(x) = \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 + \frac{1}{24}bx^4$$

For each of the systems, we will write the Hamiltonian, $\hat{H}$ and break it down into the perturbed part, $\hat{H}^{(1)}$ and the unperturbed form, $\hat{H}^{(0)}$ (or the zeroth order), for which there is an exact solution of the Schrödinger equation. Once this is determined, we will identify the zeroth order wavefunction and the zeroth order energy.

For the *anharmonic* oscillator, the Hamiltonian is:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 + \frac{1}{24}bx^4$$

The system without the perturbation is the harmonic oscillator:

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

The remaining term is the perturbation:

$$\hat{H}' = \frac{1}{6}\gamma x^3 + \frac{1}{24}bx^4$$

The zeroth order wavefunctions and the zeroth order energies are the eigenfunctions and the energies of the harmonic oscillator:

$$\psi_n^{(0)} = N_n H_n\left(\sqrt{\alpha}x\right)\cdot e^{-\frac{\alpha x^2}{2}}, \qquad \text{where} \quad \alpha = \frac{\sqrt{k\mu}}{\hbar}$$

$$E_n^{(0)} = h\nu\left(n + \tfrac{1}{2}\right), \qquad \text{where} \quad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

b. A particle in a box with the potential

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

For the particle in a box, the Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} \qquad \text{for} \qquad 0 < x < \frac{a}{2},$$

and $$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + b \qquad \text{for} \qquad \frac{a}{2} < x < a\,.$$

The unperturbed Hamiltonian is:

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}\,.$$

The perturbation is : $\hat{H}' = 0$ for $0 < x < \frac{a}{2}$

and $\hat{H}' = b$ for $\frac{a}{2} < x < a$

The zeroth order wavefunctions and the zeroth order energies are the eigenfunctions and the energies of the particle in a box:

$$\psi_n^{(0)} = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right) \qquad\qquad E_n^{(0)} = \frac{h^2 n^2}{8ma^2}$$

c. *A helium atom*

The Hamiltonian of the helium atom is the following (see course):

$$\hat{H} = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

The undisturbed Hamiltonian is the sum of the Hamiltonian of the hydrogen atom (for 2 electrons) :

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

The perturbed Hamiltonian term is the interelectronic repulsion:

$$\hat{H}' = \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

The zeroth order wave functions and the zeroth order energies are the products of hydrogen atom eigenfunctions of the two electrons and the sums of the corresponding energies, respectively:

$$\psi^{(0)}_{n\ell mn'\ell'm'} = R_{n\ell}\left(r_1\right)Y_\ell^m\left(\theta_1,\varphi_1\right)R_{n'\ell'}\left(r_2\right)Y_{\ell'}^{m'}\left(\theta_2,\varphi_2\right)$$

$$E^{(0)}_{nn'} = -\frac{m_e e^4}{2\varepsilon_0^2 h^2}\left(\frac{1}{n^2}+\frac{1}{n'^2}\right)$$

d. *A hydrogen atom in an electric field of strength E. The Hamiltonian operator for this system is*

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} + eEr\cos\theta$$

The unperturbed Hamiltonian is that of the hydrogen atom:

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

Perturbation is the term due to the electric field:

$$\hat{H}' = eEr\cos\theta$$

The zeroth order wave functions and zeroth order energies are the eigenfunctions and energies of the hydrogen atom:

$$\psi^{(0)}_{n\ell m} = R_{n\ell}\left(r\right)Y_\ell^m\left(\theta,\varphi\right)$$

$$E^{(0)}_{n} = -\frac{\mu e^4}{8\varepsilon_0^2 h^2 n^2}$$

e. *A rigid rotor with a dipole moment μ in an electric field of strength E. The Hamiltonian operator for this system is:*

$$\hat{H} = -\frac{\hbar^2}{2I}\nabla^2 + \mu E\cos\theta$$

The unperturbed Hamiltonian is that of the rigid rotor :

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2\mu}\nabla^2$$

The perturbation is the interaction of the dipole moment with the electric field:

$$\hat{H}' = \mu E \cos\theta$$

The zeroth order wave functions and zeroth order energies are the eigenfunctions and energies of the rigid rotor:

$$\psi_{\ell m}^{(0)} = Y_\ell^m(\theta,\varphi)$$

$$E_\ell^{(0)} = \frac{\hbar^2}{2I}\ell(\ell+1)$$

2. *Using a harmonic oscillator as the unperturbed problem, calculate the first order correction to the energy of the n=1 level for the system described in problem 1a. To evaluate the integrals, you can use where appropriate the raising and lowering operators that were introduced in chapter 3.*

The first-order correction of the energy of the level n is given by (average of the energy due to the perturbation):

$$E_n^{(1)} = H'_{nn} = \int_{-\infty}^{\infty} \psi_n^{(0)*}\hat{H}'\psi_n^{(0)}dx$$

where in our case :

$$\hat{H}' = \frac{1}{6}\gamma x^3 + \frac{1}{24}bx^4 \ .$$

So, we have as first-order correction of the level $n=1$:

$$E_1^{(1)} = \int_{-\infty}^{\infty} \psi_1^{(0)*}\left(\frac{\gamma}{6}x^3 + \frac{b}{24}x^4\right)\psi_1^{(0)}dx \ .$$

We can notice that the term x^3 will have zero contribution since the function is odd ($\psi_1^{(0)*}\psi_1^{(0)}$ is even and x^3 odd $\Rightarrow \psi_1^{(0)*}x^3\psi_1^{(0)}$ is odd). To evaluate the other part of the integral, let us use what we saw in chapter 3: $\hat{x} = \frac{1}{\sqrt{2\alpha}}\left(\hat{a}^+ + \hat{a}\right)$ as well as the eigenfunctions of the harmonic oscillator $\chi_n(\xi)$.

$$E_1^{(1)} = \frac{b}{24\cdot 4\alpha^2}\int_{-\infty}^{\infty}\chi_1^*\left(\hat{a}^+ + \hat{a}\right)^4\chi_1 d\xi = \frac{b}{96\alpha^2}\int_{-\infty}^{\infty}\chi_1^*\left(\hat{a}^+ + \hat{a}\right)^3\left(\sqrt{2}\chi_2 + \chi_0\right)d\xi$$

$$= \frac{b}{96\alpha^2}\int_{-\infty}^{\infty}\chi_1^*\left(\hat{a}^+ + \hat{a}\right)^2\left(\sqrt{6}\chi_3 + 3\chi_1\right)d\xi = \frac{b}{96\alpha^2}\int_{-\infty}^{\infty}\chi_1^*\left(\hat{a}^+ + \hat{a}\right)\left(2\sqrt{6}\chi_4 + 6\sqrt{2}\chi_2 + 3\chi_0\right)d\xi$$

$$= \frac{b}{96\alpha^2}\int_{-\infty}^{\infty}\chi_1^*\left(2\sqrt{30}\chi_5 + 10\sqrt{6}\chi_3 + 15\chi_1\right)d\xi = \frac{b}{96\alpha^2}\left[2\sqrt{30}\underbrace{\int_{-\infty}^{\infty}\chi_1^*\chi_5 d\xi}_{=0} + 10\sqrt{6}\underbrace{\int_{-\infty}^{\infty}\chi_1^*\chi_3 d\xi}_{=0} + 15\underbrace{\int_{-\infty}^{\infty}\chi_1^*\chi_1 d\xi}_{=1}\right]$$

$$= \frac{5b}{32\alpha^2} = \frac{5\hbar^2 b}{32k\mu}$$

3. *Using a particle-in-a-box as the perturbed problem, calculate the first-order correction to the ground state energy for the system described in problem 1b.*

Given the discontinuity of potential in $x = \frac{a}{2}$, the integral must be evaluated in two parts:

$$E_1^{(1)} = \int_{-\infty}^{\infty}\psi_1^{(0)*}\hat{H}'\psi_1^{(0)}dx = \int_0^{\frac{a}{2}}\psi_1^{(0)*}\cdot 0\cdot\psi_1^{(0)}dx + \int_{\frac{a}{2}}^{a}\psi_1^{(0)*}\cdot b\cdot\psi_1^{(0)}dx = b\cdot\int_{\frac{a}{2}}^{a}\psi_1^{(0)*}\psi_1^{(0)}dx$$

$$\overset{(*)}{=} b\cdot\frac{1}{2}\cdot\underbrace{\int_0^{a}\psi_1^{(0)*}\psi_1^{(0)}dx}_{=1} = \frac{b}{2}$$

The noted equality (*) comes from the fact that, as we have seen, the square of the proper functions $\psi_n^{(0)*}\psi_n^{(0)}$ is symmetrical (even) with respect to $x = \frac{a}{2}$. This saves us from reassessing the integral in its analytic form.

4. *Using the result of problem 1d, calculate the first-order correction to the ground state energy of a hydrogen atom in an external electric field of strength E.*

This time, we evaluate the integral in spherical coordinates, with $\hat{H}' = eEr\cos\theta$ and $\psi_{1s}^{(0)} = R_{1s}(r)Y_0^0(\theta,\varphi)$:

$$E_{1s}^{(1)} = \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi}\psi_{1s}^{(0)*}\hat{H}'\psi_{1s}^{(0)}r^2\sin\theta dr d\theta d\varphi = eE\cdot\int_0^{\infty}\left|R_{1s}(r)\right|^2 r^3 dr\int_0^{\pi}\int_0^{2\pi}\left|Y_0^0(\theta,\varphi)\right|^2\cos\theta\sin\theta d\theta d\varphi$$

$$= eE\cdot\int_0^{\infty}\left|R_{1s}(r)\right|^2 r^3 dr\int_0^{\pi}\int_0^{2\pi}\frac{1}{4\pi}\cos\theta\sin\theta d\theta d\varphi$$

By evaluating the integral on θ, we find that it is zero: $\int_0^{\pi}\cos\theta\sin\theta d\theta = \left(\tfrac{1}{2}\sin^2\theta\right)\Big|_0^{\pi} = 0$

So the first order correction for this system is $E_{1s}^{(1)} = 0$.

5. *Use first-order perturbation theory to calculate the first-order correction to the ground state energy of a quartic oscillator whose potential energy is*

$$U(x) = cx^4$$

In this case, use a harmonic oscillator as the unperturbed system. What is the perturbing potential?

Subtracting the undisturbed Hamiltonian $\hat{H}^{(0)}$ from the Hamiltonian $\hat{H}$ of the system, we obtain the expression of the perturbation $\hat{H}'$:

$$\hat{H}' = \hat{H} - \hat{H}^{(0)} = \left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + cx^4\right) - \left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right) = cx^4 - \frac{1}{2}kx^2$$

Then proceed as in Exercise 2 using the operators $\hat{a}^+$ and $\hat{a}$.

$$E_0^{(1)} = \int_{-\infty}^{\infty} \psi_0^{(0)*}\left(cx^4 - \frac{1}{2}kx^2\right)\psi_0^{(0)} dx = \frac{c}{4\alpha^2}\int_{-\infty}^{\infty} \chi_0^*\left(\hat{a}^+ + \hat{a}\right)^4 \chi_0 d\xi - \frac{k}{4\alpha}\int_{-\infty}^{\infty} \chi_0^*\left(\hat{a}^+ + \hat{a}\right)^2 \chi_0 d\xi$$

$$= \ldots = \frac{c}{4\alpha^2}\int_{-\infty}^{\infty} \chi_0^*\left(2\sqrt{6}\chi_4 + 6\sqrt{2}\chi_2 + 3\chi_0\right) d\xi - \frac{k}{4\alpha}\int_{-\infty}^{\infty} \chi_0^*\left(\sqrt{2}\chi_2 + \chi_0\right) d\xi$$

$$= \frac{3c}{4\alpha^2} - \frac{k}{4\alpha}$$