HW 6.

1. (a) $H'(x_1, x_2) = 2\beta x_1^2 x_2$ is not symmetric under particle interchange.

If H' is modified as $H'(x_1, x_2) = \beta(x_1^2 x_2 + x_2^2 x_1) = \beta x_1 x_2 (x_1 + x_2)$

then $H'(x_2, x_1) = H'(x_1, x_2)$

This modification does not depend on whether the two particles are fermions or bosons.

(b) The total wavefunction of a two-electron system contains both the spatial part and the spin part.

$$\Psi(x_1, x_2; m_1, m_2) = \phi(x_1, x_2)\, \chi(m_1, m_2)$$

where m_1, m_2 are the z-projections of the spin of the 1st or the 2nd electron.

It is more convenient to work with the numbers S and M, the total spin and its z-projection, so Ψ can also be written as

$$\Psi(x_1, x_2; S, M) = \phi(x_1, x_2)\, \chi(S, M)$$

The total wavefunction Ψ must be antisymmetric under particle interchange. For the ground state of 1D infinite square well, the spatial wavefunction is symmetric:

$$\phi(x_1, x_2) = \frac{2}{a} \sin\left(\frac{\pi x_1}{a}\right) \sin\left(\frac{\pi x_2}{a}\right)$$

The spin wavefunction χ must be antisymmetric, in order to keep the total wavefunction antisymmetric. Therefore the spin state is the singlet state

$$\chi(S, M) = \chi(S=0, M=0) = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$$

Therefore $\Psi(x_1, x_2; S, M) = \frac{2}{a}\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{a}\right)\chi(S=0, M=0)$

This is the only possible total state, so the degeneracy is 1.

(c). For two spin 1 particles, the total wavefunction must be symmetric under particle interchange. And because the spatial part $\phi(x_1, x_2) = \frac{2}{a}\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{a}\right)$ is symmetric, the spin part must also be symmetric.

Using Table 4.8 of Griffiths, possible $|SM\rangle$ states and their expansions are

SM $\quad\quad$ $s_1 m_1 \quad s_2 m_2$

$|22\rangle = |1\,1\rangle_1 |1\,1\rangle_2$ sym

$|21\rangle = \frac{1}{\sqrt{2}}|1\,1\rangle_1 |1\,0\rangle_2 + \frac{1}{\sqrt{2}}|1\,0\rangle_1 |1\,1\rangle_2$ sym

$|20\rangle = \frac{1}{\sqrt{6}}|1\,1\rangle_1 |1\,-1\rangle_2 + \sqrt{\frac{2}{3}}|1\,0\rangle_1 |1\,0\rangle_2 + \frac{1}{\sqrt{6}}|1\,-1\rangle_1 |1\,1\rangle_2$ sym

$|2\,-1\rangle = \frac{1}{\sqrt{2}}|1\,0\rangle_1 |1\,-1\rangle_2 + \frac{1}{\sqrt{2}}|1\,-1\rangle_1 |1\,0\rangle_2$ sym

$|2\,-2\rangle = |1\,-1\rangle_1 |1\,-1\rangle_2$ sym

$|1\,1\rangle = \frac{1}{\sqrt{2}}|1\,1\rangle_1 |1\,0\rangle_2 - \frac{1}{\sqrt{2}}|1\,0\rangle_1 |1\,1\rangle_2$ anti

$|1\,0\rangle = \frac{1}{\sqrt{2}}|1\,+1\rangle_1 |1\,-1\rangle_2 - \frac{1}{\sqrt{2}}|1\,-1\rangle_1 |1\,1\rangle_2$ anti

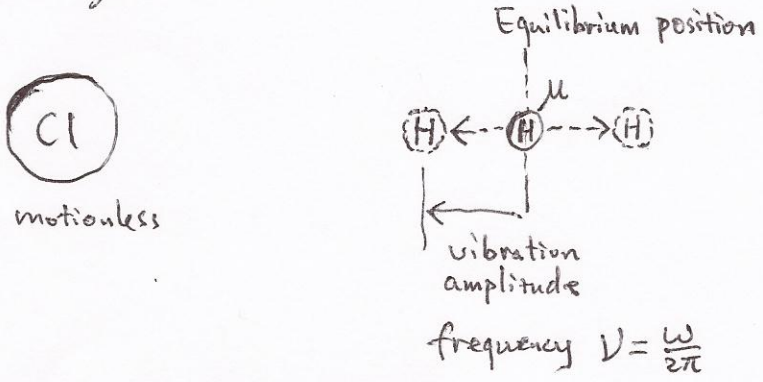
$|1\,-1\rangle = \frac{1}{\sqrt{2}}|1\,0\rangle_1 |1\,-1\rangle_2 - \frac{1}{\sqrt{2}}|1\,-1\rangle_1 |1\,0\rangle_2$ anti

$|0\,0\rangle = \frac{1}{\sqrt{3}}|1\,1\rangle_1 |1\,-1\rangle_2 - \frac{1}{\sqrt{3}}|1\,0\rangle_1 |1\,0\rangle_2 + \frac{1}{\sqrt{3}}|1\,-1\rangle_1 |1\,1\rangle_2$ sym

Among ~~them~~ there are 6 symmetric spin states. So the degeneracy is 6.

2. Problem 5.3 Griffiths

We can think of the vibrational motion of HCl as a harmonic oscillator, with the Cl atom motionless and the H atom with reduced mass μ:



frequency $\nu = \frac{\omega}{2\pi}$

The frequency of this vibration is $\nu = \frac{\omega}{2\pi}$. From quantum mechanics, this vibrational motion will emit photons with the same frequency ν.

Suppose the average mass of Cl is 36, then the reduced mass of H is

$$\mu = \frac{m_h m_{Cl}}{m_h + m_{Cl}} = \frac{1 \times 36}{1+36} = \frac{36}{37}$$

$$\nu = \frac{\omega}{2\pi} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

For $m_{Cl} = 35$ or $m_{Cl} = 37$, the vibrational frequency will be slightly different because of the slight difference in μ:

$$\mu_1 = \frac{1 \times 35}{1+35} = \frac{35}{36}, \quad \mu_2 = \frac{1 \times 37}{1+37} = \frac{37}{38}.$$

$$\nu_1 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_1}}, \quad \nu_2 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_2}}$$

$$\frac{\Delta\nu}{\nu} = \frac{\nu_1 - \nu_2}{\nu} = \frac{\frac{1}{2\pi}\sqrt{\frac{k}{\mu_1}} - \frac{1}{2\pi}\sqrt{\frac{k}{\mu_2}}}{\frac{1}{2\pi}\sqrt{\frac{k}{\mu}}} = \frac{\frac{1}{\sqrt{\mu_1}} - \frac{1}{\sqrt{\mu_2}}}{\frac{1}{\sqrt{\mu}}} = \frac{\sqrt{\frac{36}{35}} - \sqrt{\frac{38}{37}}}{\sqrt{\frac{37}{36}}} = 7.51 \times 10^{-4}$$

So $\Delta\nu = 7.51 \times 10^{-4}\nu$

3. Perturbation to infinite square well between $-a$ to a

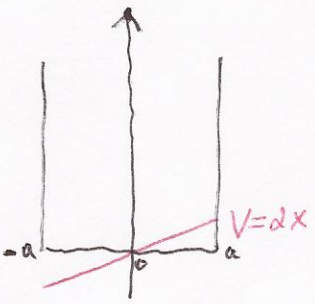
The ground state wavefunction of infinite square well between $-a$ to a is $\psi_1^0(x) = \frac{1}{\sqrt{a}}\cos\left(\frac{\pi x}{2a}\right)$

For perturbation $V_1(x) = \alpha x$

The first order correction $E_1' = \langle \psi_1^0 | V_1(x) | \psi_1^0 \rangle$

$$= \int_{-a}^{a} \psi_1^{0*}(x)\, V_1(x)\, \psi_1^0(x)\, dx$$

$$= \int_{-a}^{a} \frac{1}{a}\cos^2\left(\frac{\pi x}{2a}\right) \cdot \alpha x\, dx = 0$$



This is somehow expected because the averaged perturbation from αx is zero from $-a$ to a.

If the 1st order perturbation is zero, we go to the 2nd order:

$$E_1^2 = \sum_{m=2}^{\infty} \frac{|\langle \psi_m^0 | \alpha x | \psi_1^0 \rangle|^2}{E_1^0 - E_m^0} \qquad (*)$$

where $E_m^0 = m^2\left(\frac{\hbar^2\pi^2}{8a^2\mu}\right)$ where μ is the mass of the particle

$$\psi_m(x) = \begin{cases} \frac{1}{\sqrt{a}}\cos\left(\frac{m\pi x}{2a}\right) & \text{for } m = 1, 3, 5, 7, \cdots \\ \frac{1}{\sqrt{a}}\sin\left(\frac{m\pi x}{2a}\right) & \text{for } m = 2, 4, 6, 8, \cdots \end{cases}$$

For $m=2$, $\frac{|\langle \psi_2 | \alpha x | \psi_1 \rangle|^2}{E_1^0 - E_2^0} = \frac{\left(\frac{32a}{9\pi^2}\alpha\right)^2}{\left(\frac{\pi^2\hbar^2}{8a^2\mu}\right)\cdot(1-4)} = -0.035\left(\frac{\alpha^2 \cdot a^4 \cdot \mu}{\hbar^2}\right)$

For $m=3$, $\frac{|\langle \psi_3 | \alpha x | \psi_1 \rangle|^2}{E_1^0 - E_3^0} = 0$.

For $m=4$, $\frac{|\langle \psi_4 | \alpha x | \psi_1 \rangle|^2}{E_1^0 - E_4^0} = -0.00004488\left(\frac{\alpha^2 \cdot a^4 \cdot \mu}{\hbar^2}\right)$ this is much smaller than the case $m=2$

For $m=5$, $\frac{|\langle \psi_5 | \alpha x | \psi_1 \rangle|^2}{E_1^0 - E_5^0} = 0$.

If we terminate here at $m=5$, then

$$E_1^2 \approx (-0.035 - 0.00004488)\left(\frac{\alpha^2 a^4 \mu}{\hbar^2}\right) = -0.03504488\left(\frac{\alpha^2 a^4 \mu}{\hbar^2}\right)$$

For $V_1(x) = \alpha x^2$

$$E_1^1 = \langle \psi_1^0 | V_1(x) | \psi_1^0 \rangle = \int_{-a}^{a} \frac{1}{a}\cos^2\left(\frac{\pi x}{2a}\right)\alpha x^2 \, dx = \alpha a^2\left(\frac{\pi^2 - 6}{3\pi^2}\right)$$

$$\approx 0.13\,\alpha a^2$$

4. Stark effect for n=2 of hydrogen

For $n=2$ there are four degenerate states $\varphi_{200}, \varphi_{210}, \varphi_{211}, \varphi_{21-1}$

Perturbation : $H' = eEz$ supposing the E-field is pointing to the $+z$ direction

We need to use degenerate perturbation theory and calculate the elements of the following matrix

$$\begin{array}{c} \\ \langle\varphi_{200}| \\ \langle\varphi_{210}| \\ \langle\varphi_{211}| \\ \langle\varphi_{21-1}| \end{array} \begin{array}{c} \begin{array}{cccc} |\varphi_{200}\rangle & |\varphi_{210}\rangle & |\varphi_{211}\rangle & |\varphi_{21-1}\rangle \end{array} \\ \begin{pmatrix} \langle 200|H'|200\rangle & \cdots & & \\ \vdots & \ddots & & \\ & & & \\ & & & \end{pmatrix} \end{array}$$

There are a total of 16 matrix elements. But $\langle\psi_a|H'|\psi_b\rangle = \langle\psi_b|H'|\psi_a\rangle^*$. We only need to evaluate half of them, above the diagonal line (or below it).

$e=m=\hbar=1$ in atomic units

$$\langle 200|H'|200\rangle = eE\langle 200|z|200\rangle = eE\langle 200|r\cos\theta|200\rangle$$

$$= eE\langle R_{20}|r|R_{20}\rangle\langle Y_0^0|\cos\theta|Y_0^0\rangle \qquad Y_0^0 = \left(\frac{1}{4\pi}\right)^{\frac{1}{2}}$$

$$\text{but } \langle Y_0^0|\cos\theta|Y_0^0\rangle = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \cos\theta \cdot \frac{1}{4\pi}\cdot\sin\theta$$

$$= \frac{1}{2}\int_0^{\pi} \sin\theta\cos\theta\, d\theta = 0$$

So, $\langle 200|H'|200\rangle = 0$

$$\langle 200|H'|210\rangle = eE\langle R_{20}|r|R_{21}\rangle\langle Y_0^0|\cos\theta|Y_1^0\rangle$$

where $\langle R_{20}|r|R_{21}\rangle = \int_0^{\infty} R_{20}^*(r)\, r\, R_{21}(r)\, r^2 dr$

$$= \int_0^{\infty} \frac{1}{\sqrt{2}}\left(1-\frac{r}{2}\right)e^{-r/2}\cdot r^3\cdot\frac{1}{\sqrt{24}} r e^{-r/2} dr$$

$$= -3\sqrt{3}$$

use Table 4.7 to find the radial wave functions in atomic units Bohr radius $a=1$

$$\langle Y_0^0|\cos\theta|Y_1^0\rangle = 2\pi\int_0^\pi \left(\frac{1}{4\pi}\right)^{\frac{1}{2}}\cdot\cos\theta\cdot\left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\cos\theta\cdot\sin\theta\, d\theta = \frac{1}{\sqrt{3}}$$

So, $\langle 200|H'|210\rangle = E\langle R_{20}|r|R_{21}\rangle\langle Y_0^0|\cos\theta|Y_1^0\rangle = -3E$

And,

$\langle 200|H'|211\rangle = E\langle R_{20}|r|R_{21}\rangle\langle Y_0^0|\cos\theta|Y_1^1\rangle = 0$ ($=0$)

$\langle 200|H'|21\text{-}1\rangle = E\langle R_{20}|r|R_{21}\rangle\langle Y_0^0|\cos\theta|Y_1^{-1}\rangle = 0$ ($=0$)

Check these with Mathematica!

$\langle 210|H'|210\rangle = E\langle R_{21}|r|R_{21}\rangle\langle Y_1^0|\cos\theta|Y_1^0\rangle = 0$ ($=0$)

$\langle 210|H'|211\rangle = E\langle R_{21}|r|R_{21}\rangle\langle Y_1^0|\cos\theta|Y_1^1\rangle = 0$ ($=0$)

$\langle 210|H'|21\text{-}1\rangle = E\langle R_{21}|r|R_{21}\rangle\langle Y_1^0|\cos\theta|Y_1^{-1}\rangle = 0$ ($=0$)

$\langle 211|H'|211\rangle = E\langle R_{21}|r|R_{21}\rangle\langle Y_1^1|\cos\theta|Y_1^1\rangle = 0$ ($=0$)

$\langle 211|H'|21\text{-}1\rangle = E\langle R_{21}|r|R_{21}\rangle\langle Y_1^1|\cos\theta|Y_1^{-1}\rangle = 0$ ($=0$)

$\langle 21\text{-}1|H'|21\text{-}1\rangle = E\langle R_{21}|r|R_{21}\rangle\langle Y_1^{-1}|\cos\theta|Y_1^{-1}\rangle = 0$ ($=0$)

We have calculated all the matrix elements above the diagonal and there is only one non-zero element, namely, $\langle 200|H'|210\rangle = -3E$ in atomic units. So there are only two non-zero elements among the whole matrix. The other non-zero one is $\langle 210|H'|200\rangle = \langle 200|H'|210\rangle^* = -3E$.

So the matrix is

	$\|200\rangle$	$\|210\rangle$	$\|211\rangle$	$\|21\text{-}1\rangle$
$\langle 200\|$	0	$-3E$	0	0
$\langle 210\|$	$-3E$	0	0	0
$\langle 211\|$	0	0	0	0
$\langle 21\text{-}1\|$	0	0	0	0

So the 4×4 matrix reduces to 2×2 (red box)

Suppose the eigenvalue of this 2×2 matrix is λ

$$\begin{vmatrix} -\lambda & -3E \\ -3E & -\lambda \end{vmatrix} = \lambda^2 - 9E^2 = 0 \quad , \quad \lambda = \pm 3E$$

Therefore the originally degenerate $n=2$ state now splits into two energies, $E_2^\circ \pm 3E$. ($E_2^\circ = -3.4\ \text{eV} = -0.125$ atomic units)

If we convert the electric field $E = 100\ \text{V/cm}$ to atomic units,

$$E = 100\ \text{V/cm} = \frac{100}{5.142\times10^9}\ \text{a.u.} = 1.94\times10^{-8}\ \text{a.u.}$$

which is extremely small compared to the energy of the unperturbed $n=2$ state (-0.125 a.u.)

The final energy

For the perturbation theory to hold, the externally applied electric field must be much weaker than the internal electric field strength, i.e., the electric field felt by the electron from the proton.

This internal electric field can be estimated by assuming that the distance between the electron and the proton is a_0 (Bohr radius):

$$E_{int} = \frac{e}{4\pi\epsilon_0 a_0^2} = 5.142\times10^9\ \text{V/cm} = 1\ \text{a.u.}$$

If the externally applied electric field is close to or larger than E_{int}, then we cannot use the perturbation theory.