Answers: Problem set II

1. **(a)** For $\lambda > 0$, the first order shift in ground state energy is given by

$$\Delta E_0 = \int_{-\infty}^{\infty} \psi_0^* \lambda x^4 \psi_0 dx = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \int_{-\infty}^{\infty} dx \lambda x^4 e^{-m\omega x^2/\hbar} = \frac{3\hbar^2\lambda}{4m^2\omega^2}\,.$$

Alternatively, using the identity $x = \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger)$, we have

$$\begin{aligned}\Delta E_0 &= \lambda \left(\frac{\hbar}{2m\omega}\right)^2 \langle 0|(a+a^\dagger)^4|0\rangle \\ &= \frac{\lambda\hbar^2}{4m^2\omega^2}\langle 0|(a^2(a^\dagger)^2 + aa^\dagger aa^\dagger + a^\dagger a^2 a^\dagger)|0\rangle = \frac{3\hbar^2\lambda}{4m^2\omega^2}\,.\end{aligned}$$

(b) For $\lambda < 0$, the situation becomes more subtle. The potential now takes the form of an upturned double well potential with a metastable minimum at zero. Here, as we will see, conventional perturbative approaches fail. However, we can straightforwardly implement the WKB approach to compute the tunneling amplitude from the well created by the perturbation using the relation,

$$t \sim e^{-S}, \qquad S = \frac{1}{\hbar}\int_a^b dx\, \sqrt{2m(V(x) - E_0)}\,.$$

To implement the WKB method, we have to first identify the classical turning points.

If λ is small in magnitude, the ground state energy of the unperturbed oscillator is neglible as compared to the barrier height and we may set $E_0 = \hbar\omega/2 \simeq 0$. The classical turning points are determined by the equation $E_0 = V(x) = \frac{1}{2}m\omega^2 x^2 - \lambda x^4$. The latter has the solution at $x = a \simeq 0$ (with more care, we can show that it is simply the turning point of the harmonic oscillator, $x_0 = \sqrt{\hbar/m\omega}$) and $x = b\sqrt{m\omega^2/2\lambda}$. (The reflection about $x = 0$ also gives another set of solutions.) We therefore obtain

$$S \simeq \frac{\sqrt{2m\lambda}}{\hbar} \underbrace{\int_0^b dx\, x(b^2 - x^2)^{1/2}}_{b^3/3} = \frac{2m^2\omega^3}{3\hbar\lambda}\,,$$

which leads to the transmission probability

$$|t|^2 \sim \exp\left[-\frac{4m^2\omega^3}{3\hbar\lambda}\right]\,.$$

This result exposes the problem with perturbation theory: it assumes that the ground state energy is an analytic function of λ for some sufficiently small region around $\lambda = 0$. However, this result shows that the true ground state solution has an essential singularity in λ and the radius of convergence of the perturbation theory vanishes.

2. For a point-like nucleas, the hydrogen atom has a potential $V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$. A hollow spherical shell will have the same potential for $r > b$, but $V(r) = V(b)$ for $r < b$, by Gauss theorem, and thus its effect can be regarded as adding a perturbation,

$$\hat{H}^{(1)} = \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r} - \frac{1}{b}\right)\,,$$

to the Hamiltonian for $r < b$, and zero for $r > b$. For the $2s$ wavefunction, the energy shift induced by the perturbation is

$$\Delta E = \langle\psi|\hat{H}^{(1)}|\psi\rangle = \frac{1}{8\pi a_0^3}\frac{e^2}{4\pi\epsilon_0}\int_0^b 4\pi r^2 dr \left(\frac{1}{r} - \frac{1}{b}\right)\left(1 - \frac{r}{2a_0}\right)^2 e^{-r/a_0}\,.$$

Since $b \ll a_0$, the terms involving r/a_0 are negligible in the region of integration, so we can simplify the integral to

$$\Delta E = \frac{e^2}{8\pi\epsilon_0 a_0^3}\int_0^b r^2 dr\left(\frac{1}{r}-\frac{1}{b}\right) = \frac{b^2}{6a_0^2}R_\infty, \qquad R_\infty = \frac{e^2}{8\pi\epsilon_0 a_0}\,.$$

Likewise for the $2p_0$ wavefunction, making the same approximation, we obtain

$$\Delta E = \frac{e^2}{128\pi^2\epsilon_0 a_0^5}\int_0^b r^4\left(\frac{1}{r}-\frac{1}{b}\right)\int_0^\pi d\theta 2\pi\sin\theta\cos^2\theta = \frac{b^4}{240a_0^4}R_\infty\,.$$

Both energy shifts are very small, but that for the $2p$ state is much smaller, because the $2p$ wavefunction vanishes at the origin.

This is not a good method to explore the nucleus because other effects, such as spin-orbit interaction and other relativistic corrections would swamp the nuclear size effect. It is more effective for heavy atoms, with larger nuclei and smaller Bohr radii, and especially for "muonic" atoms, where the greater mass of the muon again reduces the Bohr radius.

3. If, without loss of generality, we take the field to lie along z, the perturbation is given by $\hat{H}' = -eEz$. At first order in perturbation theory, $\Delta E = -\langle 0|eEz|0\rangle$ vanishes since the ground state of the hydrogen atom $|0\rangle$ is an eigenstate parity. The leading contribution to ΔE is therefore the second order term $\Delta E = \sum_{k\neq 0}\frac{|\langle k|eEz|0\rangle|^2}{E_0-E_k}$. If the induced dipole moment is $\boldsymbol{d} = \alpha\epsilon_0\mathbf{E}$, its energy of interaction with the electric field is given by $\Delta E = -\frac{1}{2}\mathbf{d}\cdot\mathbf{E} = -\frac{1}{2}\alpha\epsilon_0 E^2$. So, by comparing with our perturbation theory result we obtain the required result.

An alternative derivation of this result starts from the first order perturbation theory expression for the perturbed wavefunction: $|\psi\rangle = |0\rangle + \sum_{k\neq 0} c_k|k\rangle$, where $c_k = \frac{\langle k|-eEz|0\rangle}{E_0-E_k}$. The dipole moment operator for the electron is ez, and its expectation value in this state is (neglecting small terms of order (c_k^2)),

$$\langle\psi|ez|\psi\rangle = \underbrace{\langle 0|ez|0\rangle}_{=0} + \underbrace{\sum_{k\neq 0}\left[c_k\langle 0|ez|k\rangle + c_k^*\langle k|ez|0\rangle\right]}_{2E\sum_{k\neq 0}\frac{|\langle k|ez|0\rangle|^2}{E_k-E_0}} + O(c_k^2) = \alpha\epsilon_0 E$$

from which the value of α follows as before.

Since $E_k \geq E_1$ for all k, we obtain

$$\alpha \leq \frac{2e^2}{\epsilon_0}\sum_{k\neq 0}\frac{|\langle k|z|0\rangle|^2}{E_1-E_0} = \frac{2e^2}{\epsilon_0}\sum_{k\neq 0}\frac{\langle 0|z|k\rangle\langle k|z|0\rangle}{E_1-E_0} = \frac{2e^2}{\epsilon_0}\frac{\langle 0|z^2|0\rangle}{E_1-E_0}\,,$$

where we have used the completeness relation $\mathbb{I} = \sum_k |k\rangle\langle k|$. Note that the sum now includes the $k = 0$ term. Using the explicit form for the Hydrogen ground state, $|0\rangle = (\frac{1}{\pi a_0^3})^{1/2}e^{-r/a_0}$, we evaluate the matrix element,

$$\langle 0|z^2|0\rangle = \langle 0|r^2\cos^2\theta|0\rangle = \int_0^\pi 2\pi\sin\theta\cos^2\theta d\theta\int_0^\infty r^2 dr r^2 e^{-2r/a_0} = a_0^2\,.$$

We also need the energy difference, $E_1 - E_0 = (1-\frac{1}{4})R_\infty = \frac{3}{4}\frac{e^2}{8\pi\epsilon_0 a_0}$ from which we obtain $\alpha \leq \frac{64\pi a_0^3}{3} = 9.9\times 10^{-30}\,\mathrm{m}^3$, a figure that is not too far from experiment.

4. From the trial wavefunction, we can obtained A from the normalization, $1 = \int_{-\infty}^{\infty}|\psi|^2 dx = A^2\int_{-a}^{a}(x^4 - 2a^2x^2 + a^4)dx = \frac{16}{15}A^2a^5$. Moreover, using the identity,

$$\hat{H}\psi = \left(-\frac{\hbar^2}{2m}\partial_x^2 + \frac{1}{2}m\omega^2x^2\right)\psi = A\left[\frac{\hbar^2}{m} + \frac{1}{2}m\omega^2(a^2x^2 - x^4)\right]$$

the expectation value of the Hamiltonian is given by

$$\langle\psi|\hat{H}|\psi\rangle = A^2\int_{-a}^{a}(a^2-x^2)\left[\frac{\hbar^2}{m}+\frac{1}{2}m\omega^2(a^2x^2-x^4)\right]dx = \frac{15}{8}\left[\frac{2\hbar^2}{3ma^2}+\frac{4m\omega^2a^2}{105}\right].$$

Minimising with respect to a we obtain $a^2 = (\frac{35}{2})^{1/2}\frac{\hbar}{m\omega}$. Substituting this value of a into our expression for $\langle\psi|\hat{H}|\psi\rangle$, we obtain the upper bound on the ground state energy, $\langle\psi|\hat{H}|\psi\rangle = \sqrt{\frac{5}{14}}\hbar\omega = 0.598\hbar\omega$, which is greater than the true ground state energy ($\hbar\omega/2$) as expected.

5. From the normalization, $1 = A^2\int_0^\infty 4\pi r^2 e^{-2\beta r}dr = \frac{4\pi A^2}{4\beta^3} \Rightarrow A^2 = \frac{\beta^3}{\pi}$. From the identity $\nabla^2\psi = \frac{1}{r^2}\partial_r(r^2\partial_r\psi) = \frac{1}{r^2}\partial_r(-\beta r^2 e^{-\beta r}) = \beta^2 e^{-\beta r} - \frac{2\beta}{r}e^{-\beta r}$, we have

$$\begin{aligned}\langle\psi|\hat{H}|\psi\rangle &= A^2\int_0^\infty 4\pi r^2 dr\left[-\frac{\hbar^2}{2m}\left(\beta^2 e^{-2\beta r}-\frac{2\beta}{r}e^{-2\beta r}\right)-\frac{e^2}{4\pi\epsilon_0 r}e^{-2\beta r}\right]\\ &= \frac{\hbar^2\beta^2}{2m}-\frac{e^2\beta}{4\pi\epsilon_0}.\end{aligned}$$

Minimising with respect to β we obtain $\beta = \frac{me^2}{4\pi\epsilon_0\hbar^2} = a_0^{-1}$, which is the inverse of the Bohr radius and thus $\langle\psi|\hat{H}|\psi\rangle = -\frac{m}{2\hbar^2}(\frac{e^2}{4\pi\epsilon_0})^2 = -13.6\,\text{eV}$. This is the correct value for the ground state energy of the Hydrogen atom, as expected, because we chose the correct functional form for the trial function.

6. **(a)** Suppose that the two Hamiltonians are $\hat{H}_1$ and $\hat{H}_2$ with ground state wavefunctions ψ_1 and ψ_2, i.e. $\hat{H}_1\psi_1 = E_1\psi_1$, and $\hat{H}_2\psi_2 = E_2\psi_2$. Given that $V_1 \le V_2$, we have $\hat{H}_1 = \hat{H}_2 - V_2(\mathbf{r}) + V_1(\mathbf{r}) = \hat{H}_2 + \Delta V(\mathbf{r})$. From the variational principle,

$$E_1 \le \langle\psi_2|\hat{H}_1|\psi_2\rangle = \langle\psi_2|\hat{H}_2|\psi_2\rangle - \langle\psi_2|\Delta V|\psi_2\rangle = E_2 + \langle\psi_2|\Delta V|\psi_2\rangle \le E_2,$$

where the last inequality follows because $\Delta V(\mathbf{r}) \le 0$. Thus $E_2 \ge E_1$.

(b) The Hamiltonian is given by $\hat{H} = -\frac{\hbar^2}{2m}\partial_x^2 + V(x)$, and the normalized trial function is given by $\psi = (2\lambda/\pi)^{1/4}e^{-\lambda x^2}$. Using standard integrals, we obtain $\langle\psi|\hat{H}|\psi\rangle = \frac{\hbar^2}{2m}\lambda + \sqrt{\frac{2\lambda}{\pi}}\int_{-\infty}^{\infty}dxV(x)e^{-2\lambda x^2} = \frac{\hbar^2}{2m}\lambda + I$. Minimsing with respect to λ, we obtain,

$$0 = \frac{\hbar^2}{2m}+\frac{I}{2\lambda}+\frac{I}{2\lambda}+\sqrt{\frac{2\lambda}{\pi}}\int V(x)(-2x^2)e^{-2\lambda x^2},$$

where the second term arises from differentiating the normalization in I, and the third term from differentiating the integrand. This is an implicit equation for λ and if we solve for I and substitute into the equation from above, we obtain

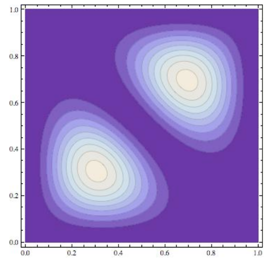
$$\langle\psi|\hat{H}|\psi\rangle = \frac{\hbar^2}{2m}\lambda + I = -\frac{\hbar^2}{2m}\lambda + 2\lambda\sqrt{\frac{2\lambda}{\pi}}\int dxV(x)(2x^2)e^{-2\lambda x^2}.$$

This is our upper bound on the ground state energy, and since $V(x) \le 0$, both terms are manifestly negative. Hence the ground state energy is negative, and at least one bound state must exist.

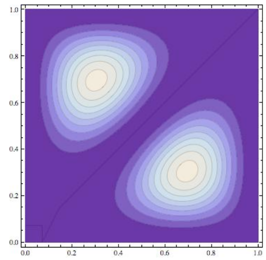
7. A single particle in the potential well has the (unnormalized) wavefunction and energy, $\psi_n(x) = \sin(n\pi x/L)$ and $E = \frac{\hbar^2\pi^2}{2mL^2}n^2 \equiv \epsilon n^2$. The wavefunction for a system of two identical particles must be either symmetric or antisymmetric, i.e.

$$\psi(x_1,x_2) = \sin(n_1\pi x_1/L)\sin(n_2\pi x_2/L) \pm \sin(n_2\pi x_1/L)\sin(n_1\pi x_2/L),$$

with energy $(n_1^2+n_2^2)\epsilon$. If $E = 5\epsilon$, we must have $n_1 = 1$, and $n_2 = 2$ (or *vice versa*).



Symmetric wavefunction



Antisymmetric wavefunction

(a) Spin-zero particles are bosons and must have a symmetric wavefunction,

$$\psi(x_1, x_2) = \sin(\pi x_1/L)\sin(2\pi x_2/L) + \sin(2\pi x_1/L)\sin(\pi x_2/L)$$
$$= 2\sin(\pi x_1/L)\sin(\pi x_2/L)\left[\cos(\pi x_1/L) + \cos(\pi x_2/L)\right] .$$

Clearly, this has zeros when $x_1 = 0,\ L$, when $x_2 = 0,\ L$, and when $x_1 + x_2 = L$.

(b) Spin 1/2 particles are fermions and must have an antisymmetric wavefunction. In the singlet case, the spin wavefunction is antisymmetric, and hence the spatial wavefunction is symmetric, just as in (a).

(c) In the triplet case, the spin wavefunction is symmetric, and hence the spatial wavefunction must be antisymmetric, i.e.

$$\psi(x_1, x_2) = \sin(\pi x_1/L)\sin(2\pi x_2/L) - \sin(2\pi x_1/L)\sin(\pi x_2/L)$$
$$2\sin(\pi x_1/L)\sin(\pi x_2/L)\left[\cos(\pi x_1/L) - \cos(\pi x_2/L)\right] .$$

Clearly, this has zeros when $x_1 = 0,\ L$, when $x_2 = 0,\ L$, and when $x_1 = x_2$. If the particles were charged, they would repel each other through the Coulomb interaction. Therefore, in the spin 1/2 case, the triplet state would have the lower energy, because the particles tend to be further apart. This is an example of the exchange interaction, and is a simplified model of what happens in the Helium atom.

8. For the single-particle states, $E = n^2 \frac{\pi^2\hbar^2}{8ma^2} = \epsilon n^2$ Since this well is not centred on zero, the single-particle eigenstates are all just proportional to $\sin(n\pi x/2a) \equiv |n\rangle$.

(a) If we write the two-particle states as $|n_1, n_2\rangle$, the ground state is $|1,1\rangle$ ($E = 2\epsilon$). The first excited states are $|2,1\rangle$ and $|1,2\rangle$ ($E = 5\epsilon$). The second excited state is $|2,2\rangle$ ($E = 8\epsilon$). The overall wavefunction needs to be symmetric for bosons, which $|1,1\rangle$ and $|2,2\rangle$ are already. These therefore pair with a symmetric spin wavefunction, which is always possible, whether or not the bosons have spin zero. For the first excited state, both symmetric and antisymmetric combinations are possible: $(|2,1\rangle \pm |1,2\rangle)/\sqrt{2}$; these would need to pair with spin wavefunctions that are respectively symmetric and antisymmetric. If $S > 0$, both are possible; if $S = 0$, only the symmetric space state is allowed.

The (normalized) ground state wavefunction is given by

$$\psi(x_1, x_2) = \langle x_1, x_2 | 1, 1\rangle = \frac{1}{a}\sin(\pi x_1/2a)\sin(\pi x_2/2a) .$$

(b) According to first order perturbation theory, the change in the ground state energy caused by $\hat{H}'$ is given by $\Delta E = \langle \hat{H}'\rangle$, where the expectation value involves the unperturbed eigenfunctions, $\Delta E = \int\int \psi^*(x_1, x_2)\hat{H}'\psi(x_1, x_2)dx_1dx_2$. Using the identity, $\int\int f(x_1, x_2)\delta(x_1 - x_2)dx_1dx_2 = \int f(x_1, x_2)dx_1$, for any function f, we have

$$\Delta E = -2aV_0 \int |\psi(x, x)|^2 dx = -\frac{2V_0}{a}\int_0^{2a} \sin^4(\pi x/2a) = -4V_0 \int_0^1 \sin^4(\pi y)dy .$$

The $\sin^4(\pi y)$ looks nasty, but written as $\sin^2(\pi y)\times\sin^2(\pi y)$, with $\sin^2(\pi y) = (1 - \cos(2\pi y))/2$, it is easily evaluated and gives $\Delta E = -3V_0/2$.