Part II: Michaelmas 2021

Advanced Quantum Mechanics Question Sheet III

Prof. S. Withington

Question 1: Perturbation Theory,Rotational dynamics: Suppose that a rigid structure, having moment of inertia I and permanent dipole moment $\mathbf{d}$, is constrained to rotate in the $x-y$ plane.

By considering $\hat{L}_z$, show that the Hamiltonian is given by

$$\hat{H}_0 = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}. \tag{1}$$

Derive the three lowest order energy eigenvalues of the freely rotating system, and their corresponding wavefunctions.

A weak, static electric field $\mathbf{E}$ is applied in the direction of the y axis. Find the matrix elements of the associated perturbation in the basis of the energy states of the freely rotating system. Present your results in terms of $|\mathbf{d}|$, I and $|\mathbf{E}|$.

Calculate to second order the new energies of the three lowest-energy states.

Are there any degeneracies, and does the perturbation split them?

Answer 1: Perturbation Theory, Rotational dynamics:
The Hamiltonian is given by

$$\begin{aligned}\hat{H} &= \frac{1}{2I}\hat{L}^2 \\ &= \frac{1}{2I}\hat{L}_z^2 \\ &= -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}.\end{aligned} \tag{2}$$

Because of the periodic nature of the solution, the corresponding energy eigenvalues and eigenfunctions become

$$\begin{aligned}E_m &= \frac{\hbar^2 m^2}{2I} \\ \psi_{\pm m}(\phi) &= \frac{1}{\sqrt{2\pi}}e^{\pm im\phi},\end{aligned} \tag{3}$$

where $m = 0, \pm 1, \pm 2, \cdots$.

The matrix elements are evaluated through

$$-\langle m'|\mathbf{d}\cdot\mathbf{E}|m\rangle = -dE\sin\phi \tag{4}$$
$$= \begin{cases} \frac{dE}{2i} & \text{for} \quad m' = m+1 \\ -\frac{dE}{2i} & \text{for} \quad m' = m-1 \\ 0 & \text{otherwise} \end{cases}$$

The first order corrections to the energies are all zero, but to second order

$$E_0 = -\frac{d^2E^2I}{2\hbar^2} \tag{5}$$
$$E_1 = \frac{\hbar^2}{2I} + \frac{d^2E^2I}{3\hbar^2}$$
$$E_2 = \frac{4\hbar^2}{2I} + \frac{d^2E^2I}{15\hbar^2}.$$

There are degeneracies, because $E_m = E_{-m}$, but these are still present in the perturbed spectrum.

Question 2: Perturbation Theory, Electron Trap: Consider an electron that is (i) constrained to move in 1D, and (ii) subject to periodic boundary conditions at $x = 0$ and $x = L$. An electron trap is introduced in the form of a small potential well having the form

$$-V_0 e^{-x^2/a^2}. \tag{6}$$

Explain why, in the absence of the perturbation, the system has degenerate states.

Show that the perturbed energy eigenvalues of degenerate pairs take the form

$$E_{n,\pm} = E_n^0 - \sqrt{\pi}V_0\frac{a}{L}\left(1 \pm e^{-k_n^2a^2}\right): \tag{7}$$

you may wish to assume that $a \ll L$.

Draw a graph to illustrate the way in which degeneracy returns as ka is increased from 0 to 2π.

Explain, without proof, how the effect of introducing the perturbation is different between the cases where (i) the unperturbed potential has periodic boundary conditions at $x = 0$ and $x = L$, and (ii) hard boundary conditions where the potential tends to $+\infty$ at $x = 0$ and $x = L$.

Answer 2: to be complete

Question 3: Perturbation Theory, Hydrogen Nucleus: The energy levels of the hydrogen atom are influenced by the finite size of the proton. A simple model of this effect is to treat the proton as a uniformly charged hollow spherical shell of radius $b = 5 \times 10^{-16}$ m.

Show that, for this model, the change in the electrostatic potential energy corresponds to introducing a perturbation

$$H^1 = \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r} - \frac{1}{b}\right) \; ; \qquad r < b \tag{8}$$

into the normal Schrödinger equation for the hydrogen atom.

Using first-order perturbation theory, estimate the energy shifts of the hydrogen 2s and 2p states, and comment on your findings.

Why is the energy shift the same for all three 2p states, and why can each of the 2s and 2p states be considered independently even though they are initially degenerate?

{ Hint: The integrals can be simplified considerably by noting that the size of the nucleus is much smaller than the atomic Bohr radius, i.e. $b \ll a_0$.

The 2s and 2p hydrogen atom wavefunctions are

$$\psi_{2s} = \sqrt{\frac{1}{8\pi a_0^3}}\left(1 - \frac{r}{2a_0}\right)e^{-r/2a_0}, \quad \psi_{2\mathrm{p}_0} = \frac{re^{-r/2a_0}}{\sqrt{32\pi a_0^5}}\cos\theta, \quad \psi_{2\mathrm{p}_{\pm 1}} = \mp\frac{re^{-r/2a_0}}{\sqrt{64\pi a_0^5}}e^{\pm i\phi}\sin\theta. \Big\} \tag{9}$$

Answer 3: From Gauss' theorem, the potential due to a hollow spherical shell of radius b carrying charge $+e$ is $V(r) = -e/4\pi\epsilon_0 r$ in the region $r > b$, and $V(r) = V(b)$ in the region $r < b$.

Compared to a pointlike charge $+e$, the effect can be regarded as adding a perturbation

$$H^1 = \begin{cases} \dfrac{e^2}{4\pi\epsilon_0}\left(\dfrac{1}{r} - \dfrac{1}{b}\right) & (r < b) \\ 0 & (r > b) \end{cases} . \tag{10}$$

For the 2s state, the energy shift induced by the perturbation H^1 is

$$(\Delta E)_{2\mathrm{s}} = \langle 2\mathrm{s}|\hat{H}^1|2\mathrm{s}\rangle = \frac{1}{8\pi a_0^3}\frac{e^2}{4\pi\epsilon_0}\int_0^b 4\pi r^2\, dr \left(\frac{1}{r}-\frac{1}{b}\right)\left(1-\frac{r}{2a_0}\right)^2 e^{-r/a_0}\,. \qquad (11)$$

Since $b \ll a_0$, the terms involving r/a_0 are negligible throughout the region of integration $0 < r < b$, so we can simplify the integral to

$$(\Delta E)_{2s} = \frac{e^2}{8\pi\epsilon_0 a_0^3}\int_0^b r^2\,\mathrm{d}r\left(\frac{1}{r}-\frac{1}{b}\right) = \frac{b^2}{6a_0^2}Ry, \qquad Ry = \frac{e^2}{8\pi\epsilon_0 a_0}\,. \qquad (12)$$

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

$$(\Delta E)_{2p_0} = \frac{e^2}{128\pi^2\epsilon_0 a_0^5}\int_0^b r^4\left(\frac{1}{r}-\frac{1}{b}\right)\mathrm{d}r\int_{-1}^{+1}\mathrm{d}\cos\theta\, 2\pi\cos^2\theta = \frac{b^4}{240a_0^4}Ry. \qquad (13)$$

The energy correction for the $2\mathrm{p}_{\pm1}$ states is the same as for the $2\mathrm{p}_0$ state:

$$(\Delta E)_{2p_{\pm1}} = \frac{e^2}{256\pi^2\epsilon_0 a_0^5}\int_0^b r^4\left(\frac{1}{r}-\frac{1}{b}\right)\mathrm{d}r\int_{-1}^{+1}\mathrm{d}\cos\theta\, 2\pi\sin^2\theta = \frac{b^4}{240a_0^4}Ry. \qquad (14)$$

A common energy correction for all the $2\mathrm{p}_m$ states is to be expected; the perturbation H^1 is isotropic, so the energy shift cannot depend on a quantum number such as m whose definition depends on a particular choice of quantisation axis (the z-axis).

The states $\{2\mathrm{s},\ 2\mathrm{p}_0,\ 2\mathrm{p}_{\pm1}\}$ are degenerate in energy, $E = -Ry/4$, so we really need to use degenerate perturbation theory. However it is easy to see that the matrix representation of H^1 in the basis of states $\{2\mathrm{s},\ 2\mathrm{p}_0,\ 2\mathrm{p}_{+1},\ 2\mathrm{p}_{-1}\}$ is diagonal just by considering the angular components of the matrix elements of H^1. The angular component of each 2s or 2p wavefunction is a spherical harmonic, Y_{00} or Y_{1m}, but the operator H^1 is independent of angle. Orthogonality of the spherical harmonics then ensures that all the off-diagonal matrix elements, $\langle 2\mathrm{p}_0|H^1|2\mathrm{s}\rangle$, $\langle 2\mathrm{p}_{\pm1}|H^1|2\mathrm{s}\rangle$, $\langle 2\mathrm{p}_{\pm1}|H^1|2\mathrm{p}_0\rangle$ and $\langle 2\mathrm{p}_{+1}|H^1|2\mathrm{p}_{-1}\rangle$, are zero. The energy corrections are therefore given simply by the diagonal matrix elements of H^1, as above.

The 2s energy shift is small, of order $(b/a_0)^2$, but the 2p energy shift is even smaller, of order $(b/a_0)^4$. This is because the 2p wavefunction vanishes at the origin (where the perturbation is) whereas the 2s wavefunction remains finite.

For light atoms, trying to measure these small energy shifts is not a good method to explore the nucleus because other effects, such as spin-orbit interactions and relativistic corrections swamp the nuclear size effect. Measuring the energy shifts is a more effective method for heavy atoms, due to the larger nuclear radius and smaller Bohr radius, and is especially effective for "muonic" atoms, where the greater mass of the muon reduces the Bohr radius by a factor ~ 200.

$\Delta E(2s) = (b^2/6a_0^2)R_\infty; \quad \Delta E(2p_0) = (b^4/240a_0^4)R_\infty.$

Question 4: Perturbation Theory, Polarizability of Hydrogen: The polarisibility of the hydrogen atom in its ground state may be estimated using perturbation theory. [The induced dipole moment in an applied electric field $\boldsymbol{E}$ is $\alpha\epsilon_0\boldsymbol{E}$ where α is the polarisibility.

Working to second order in the electric field strength, show that the energy shift in the ground state $|0\rangle$ is

$$\Delta E = (eE)^2 \sum_{k\neq 0} \frac{|\langle k|z|0\rangle|^2}{E_0 - E_k}\,, \tag{15}$$

where E_k is the unperturbed energy of state $|k\rangle$. Hence show that the polarisability is

$$\alpha = \frac{2e^2}{\epsilon_0} \sum_{k\neq 0} \frac{|\langle k|z|0\rangle|^2}{E_k - E_0}\,. \tag{16}$$

Show that the same result may be obtained from the perturbed wavefunction to first-order in $\boldsymbol{E}$ by evaluating the expectation value of the induced electric dipole moment.

Evaluation of α is tedious, but a useful upper bound may be obtained by noting that $E_k \geq E_1$, where E_1 is the energy of the first excited state. Using this observation, show that $\alpha \leq (64/3)\pi a_0^3$. Compare this upper bound with the experimental value of $\alpha = 8.5 \times 10^{-30}\,\mathrm{m}^3$.

$\Big\{$The ground state of the hydrogen atom, $|0\rangle = (\pi a_0^3)^{-1/2} e^{-r/a_0}$, will be needed to compute the matrix element $\langle 0|z^2|0\rangle$. $\Big\}$

Answer 4: Perturbation Theory: Polarizability of Hydrogen If, without loss of generality, we take the electric field to lie along z, the perturbation is given by $H^1 = eEz$. 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 of parity. The leading contribution to ΔE is therefore the second order term

$$\Delta E = \sum_{k\neq 0} \frac{|\langle k|eEz|0\rangle|^2}{E_0 - E_k}\,. \tag{17}$$

If the induced dipole moment is $\boldsymbol{d} = \alpha\epsilon_0\boldsymbol{E}$, its energy of interaction with the electric field is given by $\Delta E = -\frac{1}{2}\boldsymbol{d}\cdot\boldsymbol{E} = -\frac{1}{2}\alpha\epsilon_0 E^2$. Comparing with the perturbation theory result above then gives the polarisibility as

$$\boxed{\alpha = \frac{2e^2}{\epsilon_0} \sum_{k\neq 0} \frac{|\langle k|z|0\rangle|^2}{E_k - E_0}}\,. \tag{18}$$

An alternative derivation of this result starts from the first order perturbation theory expression for the perturbed wavefunction:

$$|\psi\rangle = |0\rangle + \sum_{k\neq 0} \frac{\langle k|eEz|0\rangle}{E_0 - E_k} |k\rangle \ . \tag{19}$$

The dipole moment operator for the electron is $-ez$, and the expectation value in this state is

$$\langle\psi|ez|\psi\rangle = \langle 0|ez|0\rangle + \sum_{k\neq 0} \left[\frac{\langle k|eEz|0\rangle}{E_0 - E_k}\langle 0|ez|k\rangle + \frac{\langle k|eEz|0\rangle^*}{E_0 - E_k}\langle k|ez|0\rangle \right] + \mathcal{O}(E^2)\,. \tag{20}$$

The first term on the right-hand side above vanishes, giving

$$\langle\psi|ez|\psi\rangle = 2E \sum_{k\neq 0} \frac{|\langle k|ez|0\rangle|^2}{E_0 - E_k} + \mathcal{O}(E^2)\,. \tag{21}$$

Comparing with $\langle\psi| - ez|\psi\rangle \equiv \alpha\epsilon_0 E$, the value of the polarisibilty α follows as before.

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

$$\alpha \leq \frac{2e^2}{\epsilon_0} \sum_{k\neq 0} \frac{|\langle k|z|0\rangle|^2}{E_1 - E_0} = \frac{2e^2}{\epsilon_0} \sum_{k\neq 0} \frac{\langle 0|z|k\rangle\langle k|z|0\rangle}{E_1 - E_0} = \frac{2e^2}{\epsilon_0} \frac{\langle 0|z^2|0\rangle}{E_1 - E_0}\,, \tag{22}$$

where we have used the completeness relation $\hat{I} = \sum_k |k\rangle\langle k|$ in the last step. Note that the completeness relation sum includes a $k = 0$ term, but this doesn't contribute because $\langle 0|z|0\rangle = 0$.

Using the explicit form for the hydrogen ground state, $|0\rangle = (\pi a_0^3)^{-1/2} e^{-r/a_0}$, we obtain

$$\langle 0|z^2|0\rangle = \langle 0|r^2\cos^2\theta|0\rangle = \int_0^\pi 2\pi \sin\theta\cos^2\theta\, d\theta \int_0^\infty r^2\, dr\, r^2 e^{-2r/a_0} = a_0^2\,. \tag{23}$$

We also need the energy difference,

$$E_1 - E_0 = \left(1 - \frac{1}{4}\right) Ry = \frac{3}{4}\frac{e^2}{8\pi\epsilon_0 a_0}\,, \tag{24}$$

from which we obtain $\alpha \leq 64\pi a_0^3/3 = 9.9 \times 10^{-30}\,\mathrm{m}^3$, not too far from experiment.

Question 5: Degenerate perturbation theory A particle of mass m is constrained to move in the xy–plane such that the Hamiltonian is given by

$$\hat{H} = \frac{1}{2m}(\hat{p}_x^2 + \hat{p}_y^2) + \frac{1}{2}m\omega^2(\hat{x}^2 + \hat{y}^2) + \lambda\hat{x}\hat{y}\,.$$

(a) Using raising and lowering operators show that for $\lambda = 0$ the (unperturbed) energy eigenvalues can be described by the equation $E_{n_x,n_y} = (n_x + n_y + 1)\hbar\omega$.

(b) For the ground state and first two excited states, describe the unperturbed eigenstates for the system in terms of one-dimensional harmonic oscillator eigenstates $|n_x\rangle$, $|n_y\rangle$. What are the degeneracies of each of these energy levels ?

(c) For the case $\lambda \neq 0$, use degenerate perturbation theory to determine the energy splitting for the lowest energy degenerate level, as well as the first-order corrections to the wavefunctions.

Answer 5: Degenerate perturbation theory

(a) For $\lambda = 0$, the Hamiltonian separates into two independent components,

$$\hat{H}^{(0)} = \hat{H}_x^{(0)} + \hat{H}_y^{(0)} \ , \tag{25}$$

each of which is a 1D harmonic oscillator of angular frequency ω.

Introducing ladder operators for x and y, the Hamiltonian can be written as

$$\hat{H}^{(0)} = \hbar\omega \left(\hat{a}_x^\dagger \hat{a}_x + \hat{a}_y^\dagger \hat{a}_y + 1\right) \ . \tag{26}$$

The overall eigenstates of $\hat{H}^{(0)}$ are products $|n_x, n_y\rangle \equiv |n_x\rangle\,|n_y\rangle$ of the individual eigenstates $|n_x\rangle$ and $|n_y\rangle$ of $\hat{H}_x^{(0)}$ and $\hat{H}_y^{(0)}$:

$$\hat{H}^{(0)}\,|n_x, n_y\rangle = (\hat{H}_x^{(0)} + \hat{H}_y^{(0)})\,|n_x\rangle\,|n_y\rangle = (E_x + E_y)\,|n_x\rangle\,|n_y\rangle = (E_x + E_y)\,|n_x, n_y\rangle \ , \tag{27}$$

where $E_x = (n_x + 1/2)\hbar\omega$ and $E_y = (n_y + 1/2)\hbar\omega$. Hence the eigenvalues of $\hat{H}^{(0)}$ are

$$\boxed{E^{(0)}_{(n_x,n_y)} = (n_x + n_y + 1)\hbar\omega} \ . \tag{28}$$

(b) The unperturbed spectrum is
$E_0^{(0)} = \hbar\omega$ with one state: $|n_x\rangle\,|n_y\rangle = |0\rangle\,|0\rangle$
$E_1^{(0)} = 2\hbar\omega$ with two states: $|n_x\rangle\,|n_y\rangle = |1\rangle\,|0\rangle\,, |0\rangle\,|1\rangle$
$E_2^{(0)} = 3\hbar\omega$ with three states: $|n_x\rangle\,|n_y\rangle = |2\rangle\,|0\rangle\,, |1\rangle\,|1\rangle\,, |0\rangle\,|2\rangle$.

(c) The perturbation is

$$\hat{H}^1 = \lambda\hat{x}\hat{y} = \lambda\frac{\hbar}{2m\omega}\left(\hat{a}_x^\dagger + \hat{a}_x\right)\left(\hat{a}_y^\dagger + \hat{a}_y\right) \ . \tag{29}$$

For the unperturbed 2-fold degenerate level with $E_1^{(0)} = 2\hbar\omega$, in the basis $\{|1,0\rangle\,, |0,1\rangle\}$, the perturbation has matrix representation

$$\hat{H}^1 = \begin{pmatrix} H^1_{11} & H^1_{12} \\ H^1_{21} & H^1_{22} \end{pmatrix} = \lambda \begin{pmatrix} \langle 1,0|\hat{x}\hat{y}|1,0\rangle & \langle 1,0|\hat{x}\hat{y}|0,1\rangle \\ \langle 0,1|\hat{x}\hat{y}|1,0\rangle & \langle 0,1|\hat{x}\hat{y}|0,1\rangle \end{pmatrix} . \tag{30}$$

Each matrix element factorises into separate x and y matrix element components:

$$\hat{H}^1 = \lambda \begin{pmatrix} \langle 1|\hat{x}|1\rangle\langle 0|\hat{y}|0\rangle & \langle 1|\hat{x}|0\rangle\langle 0|\hat{y}|1\rangle \\ \langle 0|\hat{x}|1\rangle\langle 1|\hat{y}|0\rangle & \langle 0|\hat{x}|0\rangle\langle 1|\hat{y}|1\rangle \end{pmatrix}. \tag{31}$$

The only non-zero components are

$$\langle 1|\hat{x}|0\rangle = \sqrt{\frac{\hbar}{2m\omega}}\big(\langle 1|\hat{a}_x|0\rangle + \langle 1|\hat{a}_x^\dagger|0\rangle\big) = \sqrt{\frac{\hbar}{2m\omega}} = \langle 0|\hat{x}|1\rangle\,, \tag{32}$$

and similarly for y. Hence

$$\hat{H}^1 = \lambda\frac{\hbar}{2m\omega}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{33}$$

The first-order energy corrections are given by the eigenvalues of $\hat{H}^1$. The zeroth-order eigenstates which should be used in perturbation theory are given by the eigenstates of $\hat{H}^1$. Thus the first-order energy corrections and zeroth-order eigenstates are

$$\boxed{\Delta E_1^{(1)} = \pm\frac{\lambda\hbar}{2m\omega}\,; \qquad \left|\phi_\pm^{(0)}\right\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} = \frac{1}{\sqrt{2}}\big(\,|1,0\rangle \pm |0,1\rangle\,\big)}\,. \tag{34}$$

In perturbation theory, the first-order eigenstate corresponding to the unperturbed eigenstate $\left|n^{(0)}\right\rangle$ is obtained as

$$\left|n^{(0)}\right\rangle + \sum_{E_m^{(0)}\neq E_n^{(0)}} \left|m^{(0)}\right\rangle \frac{\langle m^{(0)}|\hat{H}^1|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}\,. \tag{35}$$

Thus the first-order eigenstates corresponding to the unperturbed (zeroth-order) eigenstates $\left|\phi_\pm^{(0)}\right\rangle$, both with unperturbed energy $2\hbar\omega$, are

$$\left|\phi_\pm^{(0)}\right\rangle + \sum_{(n_x+n_y)\neq 1} |n_x,n_y\rangle \frac{\langle n_x,n_y|\lambda\hat{x}\hat{y}|\phi_\pm^{(0)}\rangle}{2\hbar\omega - E^{(0)}_{(n_x,n_y)}}\,. \tag{36}$$

Substituting for $\left|\phi_\pm^{(0)}\right\rangle$, the matrix element in the numerator is

$$\frac{\lambda}{\sqrt{2}}\big(\langle n_x,n_y|\hat{x}\hat{y}|1,0\rangle \pm \langle n_x,n_y|\hat{x}\hat{y}|0,1\rangle\big) = \frac{\lambda}{\sqrt{2}}\big(\langle n_x|\hat{x}|1\rangle\langle n_y|\hat{y}|0\rangle \pm \langle n_x|\hat{x}|0\rangle\langle n_y|\hat{y}|1\rangle\big)\,. \tag{37}$$

Expressing $\hat{x}$ and $\hat{y}$ in terms of ladder operators shows that the only non-zero contributions to the sum, with $n_x + n_y \neq 1$, come from the terms with $(n_x,n_y) = (2,1)$ or $(1,2)$, with unperturbed energy $E^{(0)}_{2,1} = E^{(0)}_{1,2} = 4\hbar\omega$:

$$\left|\phi_\pm^{(0)}\right\rangle \to \left|\phi_\pm^{(0)}\right\rangle + |2,1\rangle\,\frac{\lambda}{\sqrt{2}}\frac{\langle 2|\hat{x}|1\rangle\langle 1|\hat{y}|0\rangle}{2\hbar\omega - 4\hbar\omega} \pm |1,2\rangle\,\frac{\lambda}{\sqrt{2}}\frac{\langle 1|\hat{x}|0\rangle\langle 2|\hat{y}|1\rangle}{2\hbar\omega - 4\hbar\omega} \tag{38}$$

Using

$$\langle 2|\hat{x}|1\rangle = \sqrt{\frac{\hbar}{2m\omega}}\big(\langle 2|\hat{a}_x|1\rangle + \langle 2|\hat{a}_x^\dagger|1\rangle\big) = \sqrt{\frac{\hbar}{m\omega}}\,, \tag{39}$$

and similarly for y, then gives the first-order eigenstates as

$$\boxed{\left|\phi_{\pm}^{(0)}\right\rangle - \frac{\lambda}{4m\omega^2}\big(\,|2\rangle\,|1\rangle \pm |1\rangle\,|2\rangle\,\big).} \tag{40}$$

Question 6: Variational method Use a trial wavefunction of the form

$$\psi(x) = \begin{cases} A(a^2 - x^2) & -a < x < a \\ 0 & \text{otherwise} \end{cases} \tag{41}$$

to place an upper bound on the ground state energy of the one-dimensional harmonic oscillator with potential $V(x) = m\omega^2 x^2/2$, where m is the mass of the particle and ω is the oscillator frequency.

Compare your answer with the exact result, and comment. Why is the result slightly different to the actual ground-state energy?

Answer 6: Variational method
From the trial wavefunction, we can obtain A from the normalization,

$$1 = \int_{-\infty}^{\infty} |\psi|^2\, dx = A^2 \int_{-a}^{a} (x^4 - 2a^2x^2 + a^4)\, dx = \frac{16}{15} A^2 a^5. \tag{42}$$

Using the identity

$$\hat{H}\psi = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2\right)\psi = A\left[\frac{\hbar^2}{m} + \frac{1}{2}m\omega^2(a^2x^2 - x^4)\right]\ , \tag{43}$$

the expectation value of the Hamiltonian is given by

$$\langle\psi|\hat{H}\,|\psi\rangle = A^2 \int_{-a}^{a} (a^2 - x^2)\left[\frac{\hbar^2}{m} + \frac{1}{2}m\omega^2(a^2x^2 - x^4)\right] dx = \frac{15}{8}\left[\frac{2\hbar^2}{3ma^2} + \frac{4m\omega^2a^2}{105}\right]. \tag{44}$$

Minimising with respect to a we obtain $a^2 = (35/2)^{1/2}(\hbar/m\omega)$. Substituting this value of a into our expression for $\langle\psi|\hat{H}|\psi\rangle$, we obtain an upper bound on the ground state energy,

$$\boxed{\langle\psi|\hat{H}\,|\psi\rangle = \sqrt{(5/14)}\hbar\omega = 0.598\hbar\omega}, \tag{45}$$

which is greater than the true ground state energy $\hbar\omega/2$, as expected.

The actual ground state is Gaussian, which can be expanded to first order to give a form that is similar, but not identical, to that of the assumed formed.

Question 7: Variational method: Use variational techniques to answer the following:

(a) E_1 and E_2 are the ground state energies of a particle moving in attractive potentials $V_1(\boldsymbol{r})$ and $V_2(\boldsymbol{r})$, respectively. Using the variational method, show that $E_1 \leq E_2$ if $V_1(\boldsymbol{r}) \leq V_2(\boldsymbol{r})$.

$\Big\{$ Hint: Use the wavefunction of a particle moving in $V_2(\boldsymbol{r})$ as a trial wavefunction for the potential $V_1(\boldsymbol{r})$. $\Big\}$

(b) Consider a particle moving in a localized one-dimensional attractive potential $V(x)$, i.e. a potential such that $V(x) \leq 0$ for all x, and $V(x) \to 0$ as $|x| \to \infty$. Use the variational principle with trial function $A\exp(-\lambda x^2)$ to show that the upper bound on the ground state energy is negative, and hence that for any such potential at least one bound state must exist.

Answer 7: Variational method:
(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 $\hat{H}_2\psi_2 = E_2\psi_2$. We have $\hat{H}_1 = \hat{H}_2 - V_2(\boldsymbol{r}) + V_1(\boldsymbol{r}) = \hat{H}_2 + \Delta V(\boldsymbol{r})$, where $\Delta V(\boldsymbol{r}) \leq 0$ since $V_1(\boldsymbol{r}) \leq V_2(\boldsymbol{r})$. From the variational principle, we then obtain

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

Thus $E_1 \leq E_2$ if $V_1(\boldsymbol{r}) \leq V_2(\boldsymbol{r})$.

(b) The trial wavefunction $\psi(x) = Ae^{-\lambda x^2}$ can be normalised using a standard integral as

$$1 = |A|^2 \int_{-\infty}^{+\infty} e^{-2\lambda x^2}\,dx = |A|^2\sqrt{\frac{\pi}{2\lambda}}\,,$$

giving $\psi(x) = (2\lambda/\pi)^{1/4}e^{-\lambda x^2}$. The Hamiltonian is $\hat{H} = -(\hbar^2/2m)(d^2/dx^2) + V(x)$. Using $\psi''(x) = 4\lambda^2x^2\psi(x) - 2\lambda\psi(x)$, and the standard integral

$$\int_{-\infty}^{+\infty} x^2e^{-2\lambda x^2}\,dx = \frac{1}{4\lambda}\sqrt{\frac{\pi}{2\lambda}}\,,$$

we obtain

$$\langle\psi|\hat{H}|\psi\rangle = \frac{\hbar^2}{2m}\lambda + \sqrt{\frac{2\lambda}{\pi}}\int_{-\infty}^{\infty} V(x)e^{-2\lambda x^2}\,dx \equiv \frac{\hbar^2}{2m}\lambda + I(\lambda)\,. \tag{46}$$

Minimising with respect to λ, we obtain,

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

where the second term arises from differentiating the normalization in $I(\lambda)$, and the third term from differentiating the integrand. Solving for $I(\lambda)$ and substituting back into equation (46), we obtain

$$\langle\psi|\hat{H}|\psi\rangle = -\frac{\hbar^2}{2m}\lambda + 2\lambda\sqrt{\frac{2\lambda}{\pi}}\int_{-\infty}^{+\infty} V(x)(2x^2)e^{-2\lambda x^2}\,dx\,.$$

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

Question 8: Time-dependent perturbation theory: As shown in lectures, the probability that a system prepared in an energy eigenstate ψ_0 at time $t = 0$ is subsequently found in a state ψ_n when a weak perturbation $V(t)$ is applied is given approximately by $|c_n(t)|^2$ where

$$c_n(t) = \frac{1}{i\hbar}\int_0^t e^{i(E_n - E_0)t'/\hbar}\langle\psi_n|\hat{V}(t')|\psi_0\rangle\,\mathrm{d}t'\,.$$

where the perturbation $\hat{V}(t')$ is in the Schrödinger picture.

(i) At times $t > 0$, an electric field $\mathcal{E}_z = \mathcal{E}_0\exp(-t/\tau)$ is applied to a hydrogen atom, initially prepared in its ground state. Working to first order in the electric field, show that, after a long time, $t \gg \tau$, the probability of finding the atom in the 2s state is zero.

(ii) Likewise, show that the probability of finding the atom in the $2p_0$ state is given by

$$P(2p_0) = |c_{2p_0}(\infty)|^2 = \frac{e^2\mathcal{E}_0^2 a_0^2 2^{15}}{3^{10}}\cdot\frac{1}{\Delta E^2 + \hbar^2/\tau^2}\,.$$

Answer 8: Time-dependent perturbation theory:

(i) With $V(t) = e\mathcal{E}_0 z e^{-t/\tau}$, the amplitude for a $1s \to 2s$ transition in hydrogen is

$$c_{2s}(t) = \frac{e\mathcal{E}_0}{i\hbar}\int_0^t dt' e^{i(E_n - E_0)t'/\hbar}e^{-t'/\tau}\langle 2s|z|1s\rangle\ .$$

The matrix element $\langle 2s|z|1s\rangle = 0$, because the $1s$ and $2s$ wavefunctions both have even parity while z has odd parity. Therefore the probability of finding the atom in the $2s$ state is identically zero.

(ii) The matrix elements $\langle 2p_{\pm1}|z|1s\rangle = 0$ because the ϕ component of the integral vanishes. Therefore the probability of finding the atom in the $2p_{\pm1}$ states is identically zero.

The only non-zero matrix element is:

$$\begin{aligned}\langle 2p_0|z|1s\rangle &= \left(\frac{1}{32\pi a_0^5}\right)^{1/2}\left(\frac{1}{\pi a_0^3}\right)^{1/2}\int r^2\,dr\; r^2 e^{-r/a_0}e^{-r/2a_0}\int 2\pi\, d\cos\theta\cos^2\theta \\ &= \frac{1}{\sqrt{32}\pi a_0^4}\cdot\frac{4!}{(3/2a_0)^5}\cdot\frac{4\pi}{3} = \frac{256\,a_0}{243\sqrt{2}}\,.\end{aligned}$$

Taking the limit as $t\to\infty$, the t' integral is given by,

$$\int_0^\infty dt' e^{-t'/\tau}e^{i(E_{2p}-E_{1s})t'/\hbar} = \frac{1}{1/\tau - i\Delta E/\hbar}\,,$$

where $\Delta E = E_{2p}-E_{1s} = 3R_\infty/4$. Putting all this together we obtain the probability of being in the $2p_0$ state after a long time as

$$\boxed{P(2p_0) = |c_{2p_0}(\infty)|^2 = \frac{e^2\mathcal{E}_0^2 a_0^2 2^{15}}{3^{10}}\cdot\frac{1}{\Delta E^2+\hbar^2/\tau^2}}\,.$$

Question 9: Time-dependent perturbation theory:
A one-dimensional harmonic oscillator with Hamiltonian $\hat{H}_0 = (\hat{p}_x^2/2m) + \frac{1}{2}m\omega^2\hat{x}^2$, initially in the ground state, is subjected to a perturbation:

$$\hat{H}'(t) = \begin{cases} 0 & t<0 \text{ and } t>T \\ \lambda\hat{x}(1-t/T) & 0\le t\le T\end{cases}\,.$$

Find, to first order in λ, the probability that the oscillator is in the first excited state at time $t>T$.
Verify that for $\omega T\gg 1$ this probability approaches the value of $|\,\langle\psi_1|\psi_0'\rangle\,|^2$ where $|\psi_0'\rangle$ is the ground state for the Hamiltonian $\hat{H}_0+\lambda\hat{x}$.
$\Big\{$ The ground state and first excited state of a harmonic oscillator have wavefunctions:

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\exp\left(-\frac{m\omega}{2\hbar}x^2\right), \qquad \psi_1(x) = \left(\frac{2m\omega}{\hbar}\right)^{1/2} x\psi_0(x)\,.$$

$\Big\}$

Answer 9: Time-dependent perturbation theory:

The amplitude for a transition $0 \to n$ from the ground state is

$$c_n(t) = \frac{1}{i\hbar}\int_0^t dt' e^{i(E_n - E_0)t'/\hbar}\langle\psi_n|\hat{H}'(t')|\psi_0\rangle \ ,$$

where $E_n = (n + 1/2)\hbar\omega$.
For the perturbation

$$\hat{H}'(t) = \begin{cases} 0 & t < 0 \text{ and } t > T \\ \lambda\hat{x}(1 - t/T) & 0 \le t \le T \end{cases} \ ,$$

this gives the amplitude for a transition $0 \to 1$ to the first excited state as

$$c_1 = \frac{\lambda}{i\hbar}\int_0^T \exp(i\omega t')\left(1 - \frac{t'}{T}\right)\langle\psi_1|x|\psi_0\rangle\, dt' \ .$$

Integration by parts gives

$$c_1 = \frac{\lambda}{\hbar\omega}\langle\psi_1|x|\psi_0\rangle\left(1 + \frac{1 - \exp(i\omega T)}{i\omega T}\right) \ .$$

Using

$$\psi_1(x) = \sqrt{\frac{2m\omega}{\hbar}}x\psi_0(x) \ , \qquad \langle\psi_1|x|\psi_0\rangle = \sqrt{\frac{\hbar}{2m\omega}}$$

then gives the probability of a transition to the first excited state as

$$\boxed{|c_1|^2 = \left(\frac{\lambda}{\hbar\omega}\right)^2 \frac{\hbar}{2m\omega}\left|1 + \frac{1 - \exp(i\omega T)}{i\omega T}\right|^2} \ .$$

For $\omega T \gg 1$,

$$|c_1|^2 = \frac{\lambda^2}{2m\hbar\omega^3} \ .$$

We have

$$\hat{H}_0 + \lambda x = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 + \lambda x = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2\left(x + \frac{\lambda}{m\omega^2}\right)^2 - \frac{1}{2}\frac{\lambda^2}{m\omega^2}$$

So for the new ground state, we can use

$$x' = x + \frac{\lambda}{m\omega^2} \ .$$

We have

$$\langle\psi_1|\psi_0'\rangle = \left(\frac{2m\omega}{\hbar}\cdot\frac{m\omega}{\pi\hbar}\right)^{1/2}\int_{-\infty}^{+\infty} x\exp(-\alpha x^2 - \alpha x'^2)\, dx$$

where $\alpha = m\omega/2\hbar$. Hence

$$\langle\psi_1|\psi_0'\rangle = \left(\frac{2m\omega}{\hbar}\right)^{1/2}\left(-\frac{\lambda}{2m\omega^2}\right)\exp\left[-2\alpha\left(\frac{\lambda}{2m\omega^2}\right)^2\right] \ .$$

To first order in λ,

$$|\,\langle\psi_1|\psi_0'\rangle\,|^2 = \frac{2m\omega}{\hbar}\frac{\lambda^2}{4m^2\omega^4} = \frac{\lambda^2}{2m\hbar\omega^3} \ .$$

(Or: find an expression for ψ_0' in terms of ψ_0, ψ_1 using first order perturbation theory).