1. Liboff, problem 12.16 on page 594–595.

Consider an atom whose electrons are L–S coupled so that the good quantum numbers are $j\,\ell\,s\,m_j$ and eigenstates of the Hamiltonian H_0 may be written as $|j\,\ell\,s\,m_j\rangle$. In the presence of a uniform magnetic field $\vec{\boldsymbol{B}}$, the Hamiltonian becomes

$$H = H_0 + H' \,, \qquad \text{where} \quad H' = -\vec{\boldsymbol{\mu}}\boldsymbol{\cdot}\vec{\boldsymbol{B}} = \frac{e}{2mc}(\vec{\boldsymbol{J}} + \vec{\boldsymbol{S}})\boldsymbol{\cdot}\vec{\boldsymbol{B}} \,,$$

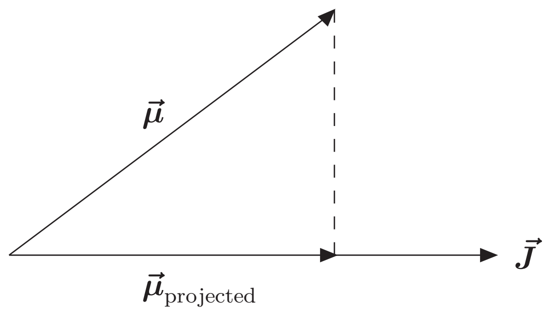
where $\vec{\boldsymbol{J}} \equiv \vec{\boldsymbol{L}} + \vec{\boldsymbol{S}}$ is the total angular momentum, $\vec{\boldsymbol{L}}$ and $\vec{\boldsymbol{S}}$ are the orbital and spin angular momenta, respectively, and $e > 0$. Before the magnetic field is turned on, $\vec{\boldsymbol{L}}$ and $\vec{\boldsymbol{S}}$ precess about $\vec{\boldsymbol{J}}$ as depicted in Fig. 12.1 on p. 580 of Liboff. Consequently,

$$\vec{\boldsymbol{\mu}} = \frac{\mu_B}{\hbar}(\vec{\boldsymbol{L}} + 2\vec{\boldsymbol{S}}) \tag{1}$$

also precesses about $\vec{\boldsymbol{J}}$, where $\mu_B \equiv e\hbar/(2mc)$ is the Bohr magneton.

After the magnetic field is turned on, if it is sufficiently weak compared to the coupling between $\vec{\boldsymbol{L}}$ and $\vec{\boldsymbol{S}}$, the ensuing precession of $\vec{\boldsymbol{J}}$ about $\vec{\boldsymbol{B}}$ is slow compared to that of $\vec{\boldsymbol{\mu}}$ about $\vec{\boldsymbol{J}}$, as depicted in Fig. 12.8a on p. 595 of Liboff.

(a) To determine the time average of $\vec{\boldsymbol{\mu}}\boldsymbol{\cdot}\vec{\boldsymbol{B}}$, we can make the following approximation. Since $\vec{\boldsymbol{\mu}}$ precesses about $\vec{\boldsymbol{J}}$ and $\vec{\boldsymbol{J}}$ precesses about $\vec{\boldsymbol{B}}$, where the latter precession is much slower than the former, then it is a good approximation to first project the vector $\vec{\boldsymbol{\mu}}$ along the direction of $\vec{\boldsymbol{J}}$ and then precess the resulting vector about $\vec{\boldsymbol{B}}$. The projection of $\vec{\boldsymbol{\mu}}$ along $\vec{\boldsymbol{J}}$ is illustrated geometrically below:



Algebraically, the projection of $\vec{\boldsymbol{\mu}}$ along $\vec{\boldsymbol{J}}$ is given by:

$$\vec{\boldsymbol{\mu}}_{\text{projected}} = (\vec{\boldsymbol{\mu}}\boldsymbol{\cdot}\hat{\boldsymbol{J}})\hat{\boldsymbol{J}} = \left(\frac{\vec{\boldsymbol{\mu}}\boldsymbol{\cdot}\vec{\boldsymbol{J}}}{\vec{\boldsymbol{J}}\boldsymbol{\cdot}\vec{\boldsymbol{J}}}\right)\vec{\boldsymbol{J}} \,,$$

where the unit vector $\hat{\boldsymbol{J}} \equiv \vec{\boldsymbol{J}}/|\vec{\boldsymbol{J}}|$. We then precess this projected vector slowly about $\vec{\boldsymbol{B}}$. That is, the time average of $\vec{\boldsymbol{\mu}}\cdot\vec{\boldsymbol{B}}$ should approximately be given by the time average of $\vec{\boldsymbol{\mu}}_{\rm projected}\cdot\vec{\boldsymbol{B}}$. Thus, we conclude that for a weak magnetic field,

$$\langle\vec{\boldsymbol{\mu}}\cdot\vec{\boldsymbol{B}}\rangle \simeq \left\langle \frac{(\vec{\boldsymbol{\mu}}\cdot\vec{\boldsymbol{J}})(\vec{\boldsymbol{J}}\cdot\vec{\boldsymbol{B}})}{\vec{\boldsymbol{J}}^2}\right\rangle . \tag{2}$$

In this argument, we have implicitly assumed that the the projection of $\vec{\boldsymbol{\mu}}$ perpendicular to $\vec{\boldsymbol{J}}$ (given by $\vec{\boldsymbol{\mu}}-\vec{\boldsymbol{\mu}}_{\rm projected}$) time-averages to zero, since the precession of $\vec{\boldsymbol{\mu}}$ about $\vec{\boldsymbol{J}}$ is so much faster than the precession of $\vec{\boldsymbol{J}}$ about $\vec{\boldsymbol{B}}$. In order to justify this assertion, one can follow Liboff's suggestion by defining:

$$\cos\alpha \equiv \hat{\boldsymbol{J}}\cdot\hat{\boldsymbol{B}}\,, \qquad \cos\beta \equiv \hat{\boldsymbol{\mu}}\cdot\hat{\boldsymbol{B}}\,, \qquad \text{and} \qquad \cos\gamma \equiv \hat{\boldsymbol{\mu}}\cdot\hat{\boldsymbol{J}}\,. \tag{3}$$

That is, α is the angle between $\vec{\boldsymbol{J}}$ and $\vec{\boldsymbol{B}}$, β is the angle between $\vec{\boldsymbol{\mu}}$ and $\vec{\boldsymbol{B}}$, and γ is the angle between $\vec{\boldsymbol{\mu}}$ and $\vec{\boldsymbol{J}}$. Liboff then observes that in the precession of $\vec{\boldsymbol{\mu}}$ about $\vec{\boldsymbol{B}}$, β varies in the range $\alpha-\gamma \leq \beta \leq \alpha+\gamma$. In particular, Liboff argues that the variation of $\cos\beta$ between its extremum values is very nearly harmonic because the angular precession of $\vec{\boldsymbol{\mu}}$ about $\vec{\boldsymbol{J}}$ is so much faster than the angular precession of $\vec{\boldsymbol{J}}$ about $\vec{\boldsymbol{B}}$. In the approximation that the variation of $\cos\beta$ is exactly harmonic,

$$\cos\beta = \cos\alpha\cos\gamma + \sin\alpha\sin\gamma\sin\omega t\,, \tag{4}$$

where ω is the angular frequency of the harmonic variation of $\cos\beta$. Indeed, since $|\sin\omega t| \leq 1$, it follows that eq. (4) yields $\alpha-\gamma \leq \beta \leq \alpha+\gamma$, after employing the identity, $\cos(\alpha\pm\gamma) = \cos\alpha\cos\gamma \mp \sin\alpha\sin\gamma$. If we take the time-average of eq. (4), and note that the precession angles α and γ are fixed in time whereas $\sin\omega t$ averages out to zero over a complete cycle, we conclude that

$$\langle\cos\beta\rangle = \langle\cos\gamma\cos\alpha\rangle\,,$$

which is equivalent to eq. (2) by virtue of eq. (3).

<u>*ADDED NOTE:*</u> Although the derivation of eq. (2) has been obtained using a classical analogy, this result turns out to be an *exact* relation in quantum mechanics when $\langle\cdots\rangle$ is reinterpreted as an expectation value with respects to eigenstates of $\vec{\boldsymbol{J}}^2$ and J_z. One can prove a rigorous theorem that states that for *any* vector operator[1] $\vec{\boldsymbol{V}}$,

$$\langle j\,,\,m_j|\,\vec{\boldsymbol{V}}\,|j\,,\,m_j\rangle = \frac{\langle j\,,\,m_j|\,\vec{\boldsymbol{V}}\cdot\vec{\boldsymbol{J}}\,|j\,,\,m_j\rangle\,\langle j\,,\,m_j|\,\vec{\boldsymbol{J}}\,|j\,,\,m_j\rangle}{j(j+1)}\,.$$

[1]A vector operator is defined as a quantum mechanical operator that rotates like a vector quantity when acted on by the rotation operator, $\exp(-i\theta\hat{\boldsymbol{n}}\cdot\vec{\boldsymbol{J}}/\hbar)$. For more details, see J.J. Sakurai, *Modern Quantum Mechanics*, 2nd edition (Addison-Wesley Publishing Company, Reading, MA, 1994), pp. 232–233.

This is known as the projection theorem.[2] Setting $\vec{\boldsymbol{V}} = \vec{\boldsymbol{\mu}}$ and taking the dot product with $\vec{\boldsymbol{B}}$ (which is a constant vector field, independent of j and m_j), one obtains eq. (2) as an exact result.

(b) We assume that the eigenstates $|j\,\ell\,s\,m_j\rangle$ are still appropriate to the perturbed Hamiltonian $H_0 + H'$. Then, using first-order perturbation theory, the shift in the energy levels due to the perturbation are given by:

$$\begin{aligned} E^{(1)} &= \langle j\,\ell\,s\,m_j|\, H'\, |j\,\ell\,s\,m_j\rangle \\ &= -\,\langle j\,\ell\,s\,m_j|\, \vec{\boldsymbol{\mu}}\boldsymbol{\cdot}\vec{\boldsymbol{B}}\, |j\,\ell\,s\,m_j\rangle \\ &= -\left\langle j\,\ell\,s\,m_j \,\middle|\, \frac{(\vec{\boldsymbol{\mu}}\boldsymbol{\cdot}\vec{\boldsymbol{J}})(\vec{\boldsymbol{J}}\boldsymbol{\cdot}\vec{\boldsymbol{B}})}{\vec{\boldsymbol{J}}^2} \,\middle|\, j\,\ell\,s\,m_j \right\rangle , \end{aligned}$$

where we have used the results of part (a), and have reinterpreted the time-average in eq. (2) as a quantum mechanical expectation value with respect to the eigenstate $|j\,\ell\,s\,m_j\rangle$ (cf. the added note following part (a) above). Using eq. (1), the above result can be written as:

$$E^{(1)} = \frac{\mu_B}{\hbar^3 j(j+1)} \langle j\,\ell\,s\,m_j|\, [(\vec{\boldsymbol{L}} + 2\vec{\boldsymbol{S}})\boldsymbol{\cdot}\vec{\boldsymbol{J}}](\vec{\boldsymbol{J}}\boldsymbol{\cdot}\vec{\boldsymbol{B}})\, |j\,\ell\,s\,m_j\rangle \ ,$$

where we have used the fact that $\vec{\boldsymbol{J}}^2\,|j\,\ell\,s\,m_j\rangle = \hbar^2 j(j+1)\,|j\,\ell\,s\,m_j\rangle$. Without loss of generality, one can choose the uniform magnetic field $\vec{\boldsymbol{B}} = B\hat{\boldsymbol{z}}$ to lie along the z-axis, in which case $\vec{\boldsymbol{J}}\boldsymbol{\cdot}\vec{\boldsymbol{B}} = BJ_z$. Using $J_z\,|j\,\ell\,s\,m_j\rangle = \hbar m_j\,|j\,\ell\,s\,m_j\rangle$, where $m_j = -j\,,\ -j+1\,,\ \ldots\,,\ j-1\,,\ j$, one obtains:

$$E^{(1)} \simeq \frac{\mu_B B m_j}{\hbar^2 j(j+1)} \langle j\,\ell\,s\,m_j|\, (\vec{\boldsymbol{L}} + 2\vec{\boldsymbol{S}})\boldsymbol{\cdot}\vec{\boldsymbol{J}}\, |j\,\ell\,s\,m_j\rangle \ . \tag{5}$$

Finally, in order to evaluate the remaining matrix element above, first recall that

$$\vec{\boldsymbol{L}}\boldsymbol{\cdot}\vec{\boldsymbol{S}} = \tfrac{1}{2}[(\vec{\boldsymbol{L}} + \vec{\boldsymbol{S}})^2 - \vec{\boldsymbol{L}}^2 - \vec{\boldsymbol{S}}^2] = \tfrac{1}{2}(\vec{\boldsymbol{J}}^2 - \vec{\boldsymbol{L}}^2 - \vec{\boldsymbol{S}}^2)\,,$$

from which one can obtain the identities:

$$\begin{aligned} \vec{\boldsymbol{L}}\boldsymbol{\cdot}\vec{\boldsymbol{J}} &= \vec{\boldsymbol{L}}\boldsymbol{\cdot}(\vec{\boldsymbol{L}} + \vec{\boldsymbol{S}}) = \vec{\boldsymbol{L}}^2 + \tfrac{1}{2}\left(\vec{\boldsymbol{J}}^2 - \vec{\boldsymbol{L}}^2 - \vec{\boldsymbol{S}}^2\right) , \\ \vec{\boldsymbol{S}}\boldsymbol{\cdot}\vec{\boldsymbol{J}} &= \vec{\boldsymbol{S}}\boldsymbol{\cdot}(\vec{\boldsymbol{L}} + \vec{\boldsymbol{S}}) = \vec{\boldsymbol{S}}^2 + \tfrac{1}{2}\left(\vec{\boldsymbol{J}}^2 - \vec{\boldsymbol{L}}^2 - \vec{\boldsymbol{S}}^2\right) . \end{aligned}$$

Hence,

$$(\vec{\boldsymbol{L}} + 2\vec{\boldsymbol{S}})\boldsymbol{\cdot}\vec{\boldsymbol{J}} = \tfrac{1}{2}\left(3\vec{\boldsymbol{J}}^2 - \vec{\boldsymbol{L}}^2 + \vec{\boldsymbol{S}}^2\right) .$$

[2] A statement of this theorem and proof can be found in J.J. Sakurai, *Modern Quantum Mechanics*, op. cit., p 241.

It follows that

$$\frac{\langle j\,\ell\,s\,m_j|\,(\vec{\boldsymbol{L}}+2\vec{\boldsymbol{S}})\boldsymbol{\cdot}\vec{\boldsymbol{J}}\,|j\,\ell\,s\,m_j\rangle}{\hbar^2 j(j+1)} = \frac{\langle j\,\ell\,s\,m_j|\,(3\vec{\boldsymbol{J}}^2-\vec{\boldsymbol{L}}^{\,2}+\vec{\boldsymbol{S}}^{2})\,\,|j\,\ell\,s\,m_j\rangle}{2\hbar^2 j(j+1)}$$

$$= \frac{3j(j+1)-\ell(\ell+1)+s(s+1)}{2j(j+1)}\,,$$

$$= 1+\frac{j(j+1)-\ell(\ell+1)+s(s+1)}{2j(j+1)}\,,$$

where we have used the fact that $\vec{\boldsymbol{S}}^2\,|j\,\ell\,s\,m_j\rangle = \hbar^2 s(s+1)\,|j\,\ell\,s\,m_j\rangle$ for a spin-s state.

It is convenient to introduce the Larmour frequency, $\Omega \equiv eB/(mc)$, in which case $\mu_B B = \frac{1}{2}\hbar\,\Omega$. We now define the *Landé g-factor*,

$$g(j\,\ell\,s) \equiv 1+\frac{j(j+1)-\ell(\ell+1)+s(s+1)}{2j(j+1)}\,.$$

Then, the first-order energy shift given by eq. (5) can be rewritten as:

$$E^{(1)} = \tfrac{1}{2}\hbar\,\Omega\,g(j\,\ell\,s)\,m_j\,, \qquad m_j = -j\,,\,-j+1\,,\,\ldots\,,\,j-1\,,\,j\,.$$

That is, the $(2j+1)$–fold degenerate unperturbed energy level has been split by the perturbation into $2j+1$ equally spaced levels.

2. The hydrogen atom is placed in a weak uniform electric field of strength $\mathcal{E}$ pointing in the z-direction. The Hamiltonian describing the system is given by:

$$H = \frac{-\hbar^2}{2m}\vec{\boldsymbol{\nabla}}^2 - \frac{e^2}{r} - e\mathcal{E}z\,.$$

Compute the ground state energy of the system using the variational technique. Use the trial wave function

$$\psi(\vec{\boldsymbol{r}}) = N(1+q\mathcal{E}z)\psi_{100}(\vec{\boldsymbol{r}})\,,$$

where $\psi_{100}(\vec{\boldsymbol{r}})$ is the ground state wave function of the hydrogen atom (in the absence of an external electric field), q is the variational parameter, and N is chosen such that the trial wave function is properly normalized. Ignore all spin effects (*i.e.*, ignore fine and hyperfine splittings). Since the external electric field is assumed to be weak, simplify your computations by expanding in $\mathcal{E}$ and keeping only the leading term. In particular, show that the first correction to the ground state energy of hydrogen is proportional to $\mathcal{E}^2$. Compare the coefficient of this term with the one obtained in class by the second-order perturbation theory calculation of the Stark effect.

First, we need to determine the normalization constant N. In spherical coordinates, $z = r\cos\theta$. Hence,

$$
\begin{aligned}
1 = \int d^3r |\psi(\vec{\boldsymbol{r}})|^2 &= \frac{|N|^2}{\pi a_0^3} \int r^2 dr d\cos\theta d\phi (1 + q\mathcal{E} r\cos\theta)^2 e^{-2r/a_0} \\
&= \frac{|N|^2}{\pi a_0^3} 2\pi \int_0^\infty r^2 e^{-2r/a_0}\, dr \int_{-1}^1 d\cos\theta (1 + q\mathcal{E} r\cos\theta)^2 \\
&= \frac{2|N|^2}{a_0^3} \int_0^\infty r^2 e^{-2r/a_0}\, dr\, \left[2 + \tfrac{2}{3} q^2\mathcal{E}^2 r^2\right] .
\end{aligned}
$$

To calculate the above integral, we make use of

$$
\int_0^\infty x^n e^{-ax}\, dx = \frac{n!}{a^{n+1}}\,, \tag{6}
$$

where n is any non-negative integer, and $a > 0$. Thus,

$$
1 = \frac{4|N|^2}{a_0^3} \left[2\left(\tfrac{1}{2}a_0\right)^2 + \tfrac{1}{3} q^2\mathcal{E}^2 \cdot 24 \left(\tfrac{1}{2}a_0\right)^5\right] = |N|^2 \left[1 + q^2\mathcal{E}^2 a_0^2\right] .
$$

Without loss of generality, one can take N to be real and positive. Thus,

$$
N = \left[1 + q^2\mathcal{E}^2 a_0^2\right]^{-1/2} .
$$

We now evaluate $E(q) \equiv \langle\psi| H |\psi\rangle$, where q is taken to be the variational parameter. Then,

$$
\begin{aligned}
E(q) &= \int d^3r\, \psi^*(\vec{\boldsymbol{r}}) \left[\frac{-\hbar^2}{2m}\vec{\boldsymbol{\nabla}}^2 - \frac{e^2}{r} - e\mathcal{E} r\cos\theta\right] \psi(\vec{\boldsymbol{r}}) \\
&= \left(\frac{1}{1 + q^2\mathcal{E}^2 a_0^2}\right) \frac{1}{\pi a_0^3} \int d^3r\, (1 + q\mathcal{E} r\cos\theta) e^{-r/a_0} \\
&\qquad\qquad \times \left[\frac{-\hbar^2}{2m}\vec{\boldsymbol{\nabla}}^2 - \frac{e^2}{r} - e\mathcal{E} r\cos\theta\right] (1 + q\mathcal{E} r\cos\theta) e^{-r/a_0} .
\end{aligned} \tag{7}
$$

For a weak electric field $\mathcal{E}$, one can expand

$$
\frac{1}{1 + q^2\mathcal{E}^2 a_0^2} \simeq 1 - q^2\mathcal{E}^2 a_0^2 . \tag{8}
$$

Moreover, using $a_0 \equiv \hbar^2/(me^2)$, we note that:

$$
\frac{1}{\pi a_0^3} \int d^3r\, e^{-r/a_0} \left[\frac{-\hbar^2}{2m}\vec{\boldsymbol{\nabla}}^2 - \frac{e^2}{r}\right] e^{-r/a_0} = -\frac{me^4}{2\hbar^2} = -\frac{e^2}{2a_0} = -1\ \mathrm{Ry}\,, \tag{9}
$$

since the integral above is just the expectation value of the hydrogen atom Hamiltonian with respect to the hydrogen ground state wave function. Thus, the value of the integral of eq. (9) is the ground state energy of hydrogen as indicated above. Using eqs. (8) and (9) to evaluate eq. (7), and keeping only terms that are quadratic in the electric field $\mathcal{E}$, one obtains

$$E(q) \simeq (1 - q^2\mathcal{E}^2 a_0^2)\Bigg[-\frac{e^2}{2a_0} - \frac{2eq\mathcal{E}^2}{\pi a_0^3}\int d^3r\, r^2\cos^2\theta\, e^{-2r/a_0}$$
$$+\frac{a^2\mathcal{E}^2}{\pi a_0^2}\int d^3r\, r\cos\theta\, e^{-r/a_0}\left[\frac{-\hbar^2}{2m}\vec{\boldsymbol{\nabla}}^2 - \frac{e^2}{r}\right] r\cos\theta e^{-r/a_0}\Bigg] + \mathcal{O}(\mathcal{E}^4)\,, \tag{10}$$

where we have noted that the $\mathcal{O}(\mathcal{E})$ term vanishes exactly due to,

$$\int_{-1}^{1}\cos\theta\, d\cos\theta = 0\,.$$

The integrals in eq. (10) are easy to evaluate. First,

$$\int d^3r\, r^2\cos^2\theta\, e^{-2r/a_0} = 2\pi\int_0^\infty r^4\, e^{-2r/a_0}\, dr\int_{-1}^{1}\cos^2\theta\, d\cos\theta = 2\pi\,(24)\left(\tfrac{1}{2}a_0\right)^5\left(\tfrac{2}{3}\right) = \pi a_0^5\,,$$

after making use of eq. (6). Second, for any function of r and θ that is independent of ϕ,

$$\begin{aligned}
\vec{\boldsymbol{\nabla}}^2 f(r,\theta) &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(\frac{\partial f}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial f}{\partial\theta}\right)\\
&= \frac{1}{r^2}\frac{\partial}{\partial r}\left(\frac{\partial f}{\partial r}\right) + \frac{1}{r^2}\frac{\partial}{\partial\cos\theta}\left[(1-\cos^2\theta)\,\frac{\partial f}{\partial\cos\theta}\right]\\
&= \frac{\partial^2 f}{\partial r} + \frac{2}{r}\frac{\partial f}{\partial r} + \frac{1}{r^2}\frac{\partial^2 f}{\partial(\cos\theta)^2} - \frac{2\cos\theta}{r^2}\frac{\partial f}{\partial\cos\theta}\,,
\end{aligned} \tag{11}$$

where we have used $d\cos\theta = -\sin\theta d\theta$ and $\sin^2\theta = 1-\cos^2\theta$. In the last line above,

$$\frac{\partial^2 f}{\partial(\cos\theta)^2} \equiv \frac{\partial}{\partial\cos\theta}\left(\frac{\partial f}{\partial\cos\theta}\right)\,.$$

Using the results of eq. (11), one may compute:

$$\begin{aligned}
\vec{\boldsymbol{\nabla}}^2(r\cos\theta\, e^{-r/a_0}) &= \cos\theta\left[\frac{\partial}{\partial r}\left(e^{-r/a_0} - \frac{r}{a_0}e^{-r/a_0}\right) + \frac{2}{r}\left(e^{-r/a_0} - \frac{r}{a_0}e^{-r/a_0}\right) - \frac{2}{r}\,e^{-r/a_0}\right]\\
&= -\frac{4}{a_0}\cos\theta\, e^{-r/a_0} + \frac{r}{a_0^2}\cos\theta\, e^{-r/a_0}\\
&= \frac{1}{a_0^2}\cos\theta\, e^{-r/a_0}(r-4a_0)\,.
\end{aligned} \tag{12}$$

Using the results of eq. (12),

$$\int d^3r\, r\cos\theta\, e^{-r/a_0}\, \vec{\boldsymbol{\nabla}}^2 \left(r\cos\theta\, e^{-r/a_0}\right) = \frac{2\pi}{a_0^2}\int_0^\infty r^3(r-4a_0)e^{-2r/a_0}\,dr \int_{-1}^1 \cos^2\theta\, d\cos\theta$$

$$= \frac{2\pi}{a_0^2}\left[24\left(\tfrac{1}{2}a_0\right)^5 - 4a_0\cdot 6\left(\tfrac{1}{2}a_0\right)^4\right]\left(\tfrac{2}{3}\right) = -\pi a_0^3\,.$$

Finally,

$$\int d^3r\, r\cos^2\theta\, e^{-2r/a_0} = 2\pi\int_0^\infty r^3\, e^{-2r/a_0}\,dr \int_{-1}^1 \cos^2\theta\, d\cos\theta = (2\pi)\cdot 6\left(\tfrac{1}{2}a_0\right)^4\left(\tfrac{2}{3}\right) = \tfrac{1}{2}\pi a_0^4\,.$$

Inserting the integrals computed above into eq. (10), we end up with:

$$E(q) = (1-q^2\mathcal{E}^2a_0^2)\left[-\frac{e^2}{2a_0} - 2eq\mathcal{E}^2a_0^2 + \frac{\hbar^2q^2\mathcal{E}^2}{2m} - \tfrac{1}{2}e^2q^2\mathcal{E}^2a_0^2\right] + \mathcal{O}(\mathcal{E}^4)\,. \tag{13}$$

One can simplify this result by noting that the definition of the Bohr radius, $a_0 = \hbar^2/(me^2)$, implies the relation:

$$\frac{\hbar^2}{2m} = \tfrac{1}{2}e^2a_0\,.$$

Inserting this result into eq. (13), one sees that the last two terms of eq. (13) cancel and we are left with:

$$E(q) = (1-q^2\mathcal{E}^2a_0^2)\left(-\frac{e^2}{2a_0} - 2eq\mathcal{E}^2a_0^2\right) + \mathcal{O}(\mathcal{E}^4)$$

$$= -\frac{e^2}{2a_0} - \tfrac{1}{2}ea_0\mathcal{E}^2q(4a_0 - eq) + \mathcal{O}(\mathcal{E}^4)\,. \tag{14}$$

We now minimize $E(q)$ by taking the derivative with respect to q and setting the result to zero.

$$\frac{dE(q)}{dq} = 0 \quad\Longrightarrow\quad q = \frac{2a_0}{e}\,.$$

Inserting $q = 2a_0/e$ back into eq. (14) yields the variational estimate for the ground state energy E in the presence of a weak uniform electric field $\mathcal{E}$:

$$E = -\frac{e^2}{2a_0} - 2a_0^3\mathcal{E}^2 = E^{(0)} - 2a_0^3\mathcal{E}^2\,,$$

where $E^{(0)}$ is the (unperturbed) ground state energy when the external electric field is absent.

In class, we used stationary state perturbation theory to show that the first-order energy shift vanishes and the second-order energy shift is given by:

$$E^{(2)} = -\tfrac{9}{4}a_0^3\mathcal{E}^2\,. \tag{15}$$

The variational computation comes pretty close. As expected, the energy evaluated by the variational principle is *larger* than the true answer, since $-2 > -\frac{9}{4}$. Keep in mind that in order to derive eq. (15), we needed to find a very clever method that effectively sums over all the energy eigenstates in the formula for the second-order energy shift. Without access to this technique, we showed in class how to bound the second-order energy shift, which resulted in

$$-\left(\tfrac{8}{3}\right)\mathcal{E}^2 a_0^2 \leq E^{(2)} \leq -0.55\left(\tfrac{8}{3}\right)\mathcal{E}^2 a_0^2\,.$$

(See also problem 13.11 of Liboff on pp. 691–692, where the upper bound to the second-order energy shift is computed.) Note that both the exact second-order energy shift and the variational energy shift fall within these bounds. Finally, we note that one additional advantage of the variational approach is that it permits us to compute the energy shift even if the external electric field $\mathcal{E}$ is not weak!

3. Liboff, problem 13.43 on page 735.

A one-dimensional harmonic oscillator in the ground state is acted upon by a uniform electric field,

$$\mathcal{E}(t) = \frac{\mathcal{E}_0}{\sqrt{\pi}}\exp\left[-\left(\frac{t}{\tau}\right)^2\right], \tag{16}$$

switched on at $t = -\infty$. The field is parallel to the axis of the oscillator. To compute the probability that the oscillator suffers a transition from the ground state to the first excited state at $t = \infty$, In Section 13.5 of Liboff, we see that if the time-dependent Hamiltonian takes the form:

$$H(\vec{\boldsymbol{r}}, t) = H^{(0)}(\vec{\boldsymbol{r}}) + H'(\vec{\boldsymbol{r}}, t)\,, \qquad \text{where}\;\; H'(\vec{\boldsymbol{r}}, t) = \mathbb{H}'(\vec{\boldsymbol{r}})f(t)\,, \tag{17}$$

then the probability of a transition from state n to state $k \neq n$ is given, to first-order in time-dependent perturbation theory, by eq. (13.52) of Liboff on p. 711,

$$P_{n\to k} = \frac{|\left\langle n^{(0)}\right|\mathbb{H}'(\vec{\boldsymbol{r}})\left|k^{(0)}\right\rangle|^2}{\hbar^2}\left|\int_{-\infty}^{\infty} e^{i\omega_{kn}t'}f(t')dt'\right|^2, \tag{18}$$

where $\hbar\omega_{kn} \equiv E_k^{(0)} - E_n^{(0)}$ is the difference between unperturbed energies, and the superscript 0 refers to the energy eigenstates and energy eigenvalues of the unperturbed Hamiltonian $H^{(0)}$.

In this problem, the perturbation is given by:

$$H'(x, t) = -qx\mathcal{E}(t)\,,$$

where q is the charge of the harmonic oscillator and $\mathcal{E}(t)$ is given by eq. (16) In the notation of eq. (17), $f(t) = \exp(-t^2/\tau^2)$ and $\mathbb{H}'(x) = -qx\mathcal{E}_0/\sqrt{\pi}$. Applying the results of eq. (18), we first compute the integral,

$$\int_{-\infty}^{\infty} e^{i\omega t}e^{-t^2/\tau^2}\,dt\,.$$

Setting $\xi \equiv t/\tau$, we can rewrite the integral above as

$$\tau \int_{-\infty}^{\infty} e^{i\omega\tau\xi} e^{-\xi^2}\, d\xi = \tau e^{-\tau^2\omega^2/4} \int_{-\infty}^{\infty} \exp\left[-\left(\xi - \tfrac{1}{2}i\omega\tau\right)^2\right] d\xi\,,$$

which is a consequence of the algebraic identity (called "completing the square"):

$$i\omega\tau\xi - \xi^2 = -\left(\xi - \tfrac{1}{2}i\omega\tau\right)^2 - \tfrac{1}{4}\omega^2\tau^2\,.$$

We change variables once more by introducing $\xi' \equiv \xi - \frac{1}{2}i\omega\tau$. The limits of integration change to a straight-line contour in the complex plane that starts at $-\infty - \frac{1}{2}i\omega\tau$ and ends at $\infty - \frac{1}{2}i\omega\tau$. However, from the theory of complex analysis, we know that it is permissible to deform the contour as long as the contour does not cross any singularities of the integrand. Since $\exp(-\xi'^{,2})$ is an analytic function, we can move the contour back to the real axis without changing the value of the integral. Hence,

$$\begin{aligned}
\int_{-\infty}^{\infty} e^{i\omega t} e^{-t^2/\tau^2}\, dt &= \tau e^{-\tau^2\omega^2/4} \int_{-\infty}^{\infty} \exp\left[-\left(\xi - \tfrac{1}{2}i\omega\tau\right)^2\right] d\xi \\
&= \tau e^{-\tau^2\omega^2/4} \int_{-\infty}^{\infty} e^{-\xi'^{\,2}}\, d\xi' \\
&= \sqrt{\pi}\tau e^{-\tau^2\omega^2/4}\,.
\end{aligned}$$

Next, we need to evaluate the matrix element of $\mathbb{H}'(x)$ between the $n = 0$ and $n = 1$ energy eigenstates of the simple one-dimensional harmonic oscillator:

$$\langle 0|\, \mathbb{H}'\, |1\rangle = -\frac{q\mathcal{E}_0}{\sqrt{\pi}} \langle 0|\, x\, |1\rangle\,.$$

In class, we derived:

$$\langle n|\, x\, |k\rangle = \left(\frac{\hbar}{2m\omega_0}\right)^{1/2} \left[\sqrt{k}\, \delta_{n,k-1} + \sqrt{k+1}\, \delta_{n,k+1}\right]\,, \tag{19}$$

where ω_0 is the unperturbed angular frequency of the oscillator. Taking $n = 0$ and $k = 1$,

$$\langle 0|\, x\, |1\rangle = \left(\frac{\hbar}{2m\omega_0}\right)^{1/2}\,.$$

Thus,

$$\langle 0|\, \mathbb{H}'\, |1\rangle = -\frac{q\mathcal{E}_0}{\sqrt{\pi}} \left(\frac{\hbar}{2m\omega_0}\right)^{1/2}\,.$$

Using the results obtained above, and noting that the energy difference between the $n = 1$ and $n = 0$ states of the harmonic oscillator is $\hbar\omega_{10} = \hbar\omega_0$, we find:

$$P_{0\to 1} = \frac{|\, \langle 0|\, \mathbb{H}'(x)\, |1\rangle\, |^2}{\hbar^2} \left| \int_{-\infty}^{\infty} e^{i\omega_{10}t'} e^{-t'^{\,2}/\tau^2} dt' \right|^2 = \frac{q^2\mathcal{E}_0^2\tau^2}{2m\hbar\omega_0}\, e^{-\omega_0^2\tau^2/2}\,. \tag{20}$$

We now consider two limiting cases.

(a) $\omega_0\tau \gg 1$.

In this limit, the transition probability, $P_{0\to 1}$ is exponentially suppressed, and the harmonic oscillator remains in its ground state. This is an example of adiabatic perturbation, in which the time-scale over which the perturbation changes is very long.

(b) $\omega_0\tau \approx 1$.

In this limit, the perturbation is not adiabatic, as the time-scale over which the perturbation changes is of order the natural time scale of the system. The probability of a transition from the ground state to the first excited state is non-negligible. However, keep in mind that if $P_{0\to 1}$ must still be small as compared to 1 if the perturbation theory result is to be reliable.

In case (b), there are no first-order transitions from the ground state to excited states of the oscillator with quantum number $k \geq 2$. This is a consequence of eq. (19), which indicates that $\langle 0|\, x\, |k\rangle = 0$ for $k \geq 2$. However, when higher orders of perturbation theory are taken into account, one does find that transitions from the ground state to excited states of the oscillator with quantum number $k \geq 2$ are possible. For this particular problem, one can actually solve the time-dependent Schrodinger equation exactly, and compute $P_{0\to k}$ for any value of k. The general result is quite interesting, and I quote it here:[3]

$$P_{0\to k} = e^{-P}\,\frac{P^k}{k!}\,, \qquad \text{where} \quad P = \frac{q^2\mathcal{E}_0^2\tau^2}{2m\hbar\omega_0}\,e^{-\omega_0^2\tau^2/2}\,, \tag{21}$$

for any non-negative integer k. We recognize eq. (21) as describing a Poisson distribution. Note that the total probability for either no transition or some transition must be equal to 1. This is easily verified:

$$\sum_0^\infty P(0\to k) = e^{-P}\sum_0^\infty \frac{P^k}{k!} = e^{-P}e^{P} = 1\,.$$

To see that this general result is consistent with our first-order perturbation theory computation, we note that if $P \ll 1$, then one can approximate $e^{-P} \simeq 1$, in which case one sees from eqs. (20) and (21) that $P_{0\to 1} \simeq P$ as required (and $P(0\to k)$ for $k \geq 2$ is negligible). Moreover, in this limit, the probability of no transition is given by $P_{0\to 0} = e^{-P} \simeq 1 - P = 1 - P_{0\to 1}$, as expected.[4] If the condition $P \ll 1$ does not hold, then the first-order perturbative result given in eq. (20) is unreliable.

[3] See e.g., A. Galindo and P. Pascual *Quantum Mechanics II* (Springer-Verlag, Berlin, Germany, 1991), section 11.3.

[4] Here, we need to be a little more accurate in our estimate of e^{-P} for $P \ll 1$, since we know that the total probability for either no transition or some transition must be equal to 1.

4. Liboff, problem 13.44 on page 735.

Radioactive tritium H^3 decays to light helium (He^{3+}) with the emission of an electron. This electron quickly leaves the atoms and may be ignored in the following calculation. The effect of the β-decay is to change the nuclear charge at $t = 0$ without effecting any change in the orbital electron. This is an example of a sudden time-dependent perturbation.

We assume that the atom is initially in its ground state. In order to compute the probability that the He^+ ion is left in the ground state of the decay, we note that the wave function of the He^+ ion just after the β-decay is the same as the wave function of the tritium H^3 just before the decay. This must be true, since the wave function does not have time to re-adjust as the sudden perturbation occurs over a time-scale much shorter than any of the natural time-scales of the atomic system.

Let $\psi_{\rm H}(r)$ be the wave function of the ground state of tritium, and let $\psi_{\rm He}(r)$ be the wave function of the ground state of the He^+ ion. For any hydrogen-like atom with nuclear charge Ze, the ground state wave function is given by:

$$\psi(r) = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/a_0} \,. \tag{22}$$

For tritium, $Z = 1$ and for the He^+ ion, $Z = 2$. To determine the probability that the He^+ ion is in its ground state, one must expand the He^+ ion wave function with respect to the He^+ ion energy eigenstates,[5]

$$|\psi\rangle = \sum_{n,\ell,m_\ell}^{\infty} |n\,\ell\,m_\ell\rangle\,\langle n\,\ell\,m_\ell|\,\psi\rangle\,.$$

The ground state corresponds to $(n\,,\,\ell\,,\,m_\ell) = (1\,,\,0\,,\,0)$. Thus, the probability that the He^+ ion is in its ground state is simply $|\,\langle 1\,0\,0|\,\psi\rangle|^2$. As noted above, $|\psi\rangle$ in the coordinate representation is given by eq. (22) with $Z = 1$, and $|1\,0\,0\rangle$ is given in the coordinate representation is given by eq. (22) with $Z = 2$. Hence, the probability that the He^+ ion is in its ground state is given by:

$$|\,\langle 1\,0\,0|\,\psi\rangle|^2 = \left|\frac{2\sqrt{2}}{\pi a_0^3}\int d^3r\, e^{-3r/a_0}\right|^2 .$$

The integral above is easily evaluated:

$$\int d^3r\, e^{-3r/a_0} = 4\pi\int_0^\infty r^2 e^{-3r/a_0}\,dr = (4\pi)\cdot 2!\,\left(\tfrac{1}{3}\right)^3 a_0^3 = \frac{8\pi}{27}\,a_0^3\,.$$

Thus, the probability that the He^+ ion is in its ground state is:

$$|\,\langle 1\,0\,0|\,\psi\rangle|^2 = \left(\frac{16\sqrt{2}}{27}\right)^2 = \frac{512}{729} \simeq 0.70\,.$$

[5]We neglect electron spin here, although this plays no role in the computation.

5. Liboff, problem 14.7 on page 782.

Consider the scattering of particles of mass m from the attractive Gaussian potential,

$$V(r) = -V_0 \exp\left[-\left(\frac{r}{a}\right)^2\right] .$$

The scattering amplitude, $f(\theta)$, for the scattering by a central potential in the Born approximation, is given by eq. (14.37) on p. 780 of Liboff,

$$f(\theta) = -\frac{2m}{\hbar^2 K}\int_0^\infty dr\, rV(r)\sin Kr\,, \qquad \text{where} \quad K \equiv 2k\sin(\theta/2)\,,$$

and θ is the scattering angle. Thus, we must compute:

$$f(\theta) = \frac{2mV_0}{\hbar^2 K}\int_0^\infty dr\, re^{-r^2/a^2}\sin Kr\,.$$

Note that the integrand is an even function of r, so we can rewrite it as:[6]

$$f(\theta) = \frac{mV_0}{\hbar^2 K}\int_{-\infty}^\infty dr\, re^{-r^2/a^2}\sin Kr\,. \tag{23}$$

The easiest way to evaluate this integral is to make use of $\sin Kr = \text{Im}\ e^{iKr}$. Then, employing the "completing the square" technique illustrated in the solution to problem 4,

$$\begin{aligned}
f(\theta) &= \frac{mV_0}{\hbar^2 K}\,\text{Im}\int_{-\infty}^\infty dr\, re^{-r^2/a^2}e^{iKr} \\
&= \frac{mV_0}{\hbar^2 K}e^{-K^2a^2/4}\,\text{Im}\int_{-\infty}^\infty dr\, r\exp\left[-\left(\tfrac{r}{a}-\tfrac{1}{2}iKa\right)^2\right] \\
&= \frac{mV_0a^2}{\hbar^2 K}e^{-K^2a^2/4}\,\text{Im}\int_{-\infty}^\infty d\xi\,\left(\xi+\tfrac{1}{2}iKa\right)e^{-\xi^2} \\
&= \frac{mV_0a^3}{2\hbar^2}e^{-K^2a^2/4}\int_{-\infty}^\infty d\xi\, e^{-\xi^2} \\
&= \frac{mV_0a^3\sqrt{\pi}}{2\hbar^2}e^{-K^2a^2/4}\,,
\end{aligned} \tag{24}$$

where we changed the integration variable to $\xi \equiv \frac{r}{a} - \frac{1}{2}iKa$ and deformed the contour of integration to lie along the real ξ-axis.

[6] Even though the radial variable r is non-negative, in evaluating the integral above, there is no mathematical reason that prevents us from rewriting the integral in the form of eq. (23).

The differential cross-section for a particle with energy $E = \hbar^2 k^2/(2m)$, following eq.(14.6) on p. 765 of Liboff, is given by:

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 \,.$$

Hence, eq. (24) yields:

$$\frac{d\sigma}{d\Omega} = \frac{\pi m^2 V_0^2 a^6}{4\hbar^4} e^{-2k^2a^2\sin^2(\theta/2)} \,,$$

after substituting $K \equiv 2k\sin(\theta/2)$. The total cross-section is given by

$$\begin{aligned}
\sigma = \int \frac{d\sigma}{d\Omega}\, d\Omega = 2\pi \int_{-1}^{1} \frac{d\sigma}{d\Omega}\, d\cos\theta \\
= \frac{\pi^2 m^2 V_0^2 a^6}{2\hbar^4} \int_{-1}^{1} e^{-2k^2a^2\sin^2(\theta/2)}\, d\cos\theta \\
= \frac{\pi^2 m^2 V_0^2 a^6}{2\hbar^4} \int_{-1}^{1} e^{-k^2a^2(1-w)}\, dw \,,
\end{aligned}$$

where $w \equiv \cos\theta$. In performing the last step above, we have used the identity, $\sin^2(\theta/2) = \frac{1}{2}(1 - \cos\theta)$. The last integral above is easily obtained:

$$\int_{-1}^{1} e^{-k^2a^2(1-w)}\, dw = e^{-k^2a^2} \int_{-1}^{1} e^{wk^2a^2}\, dw = \frac{1}{k^2a^2}\left(1 - e^{-2k^2a^2}\right) \,.$$

Hence, the total cross-section in the Born approximation is given by:

$$\sigma = \frac{\pi^2 m^2 V_0^2 a^4}{2\hbar^4 k^2}\left(1 - e^{-2k^2a^2}\right) \,.$$