1. As promised, here is the trick for summing the matrix elements for the Stark effect for the ground state of the hydrogen atom.

Recall, we need to calculate the correction to the ground state energy to second order in the perturbation due to an external field. This correction is

$$\Delta E_1 = e^2 E^2 \sum_{m=2}^{\infty} \frac{|\langle m,1,0 \mid z \mid 1,0,0\rangle|^2}{E_1 - E_m} .$$

To simplify the notation, lets call $|1,0,0\rangle = |0\rangle$, the ground state with energy E_0 and call $|m,1,0\rangle = |n\rangle$ with energy E_n and $n \ge 1$. So, we want to compute

$$\Delta E_0 = e^2 E^2 \sum_{n=1}^{\infty} \frac{|\langle n \mid z \mid 0\rangle|^2}{E_0 - E_n} .$$

(a) Suppose we had an operator A such that

$$z\,|0\rangle = (AH_0 - H_0 A)\,|0\rangle \ , \tag{1}$$

where H_0 is the unperturbed Hamiltonian for the hydrogen atom,

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{r} ,$$

where m is the reduced mass of the electron and proton. Show that

$$\langle n \mid z \mid 0\rangle = (E_0 - E_n)\,\langle n \mid A \mid 0\rangle \ .$$

Also show that

$$\sum_{n=1}^{\infty} \frac{|\langle n \mid z \mid 0\rangle|^2}{E_0 - E_n} = \langle 0 \mid zA \mid 0\rangle - \langle 0 \mid z \mid 0\rangle\,\langle 0 \mid A \mid 0\rangle = \langle 0 \mid zA \mid 0\rangle \ .$$

Solution

$$\langle n \mid z \mid 0\rangle = \langle n \mid AH_0 \mid 0\rangle - \langle n \mid H_0 A \mid 0\rangle = (E_0 - E_n)\,\langle n \mid A \mid 0\rangle \ ,$$

Since H_0 is Hermitian. Also,

$$\begin{aligned}
\sum_{n=1}^{\infty} \frac{|\langle n \mid z \mid 0\rangle|^2}{E_0 - E_n} &= \sum_{n\neq 1} \frac{\langle 0 \mid z \mid n\rangle\,(E_0 - E_n)\,\langle n \mid A \mid 0\rangle}{E_0 - E_n} \\
&= \sum_{n\neq 1} \langle 0 \mid z \mid n\rangle\,\langle n \mid A \mid 0\rangle \\
&= \sum_{n} \langle 0 \mid z \mid n\rangle\,\langle n \mid A \mid 0\rangle - \langle 0 \mid z \mid 0\rangle\,\langle 0 \mid A \mid 0\rangle \\
&= \langle 0 \mid zA \mid 0\rangle - \langle 0 \mid z \mid 0\rangle\,\langle 0 \mid A \mid 0\rangle \\
&= \langle 0 \mid zA \mid 0\rangle \ ,
\end{aligned}$$

where the second term has been dropped, since $\langle 0 \mid z \mid 0 \rangle = 0$.

End Solution

(b) So, if we knew A, we could get the answer just by calculating one matrix element. If we assume A is a function only of coordinates, then equation (1) is an inhomogeneous differential equation for A. If you're really good at differential equations, you could solve it. The result is

$$A = -\frac{ma}{\hbar^2}\left(\frac{r}{2} + a\right) z \, .$$

Show that this expression does, in fact, solve equation (1). (Note that the normalization of $|0\rangle$ cancels out, so you can just take $|0\rangle = \exp(-r/a)$.)

Solution

We need to calculate

$$-\left(-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) - \frac{\hbar^2}{2mr^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{e^2}{r}\right) \left(-\frac{ma}{\hbar^2}\left(\frac{r^2}{2} + ar\right)\cos\theta \, e^{-r/a}\right) \, .$$

This is the second term on the right hand side of equation (1). There may be some ways to simplify this, but in the end, it appears brute force is required, so, we'll just evaluate each term. First of all, the second derivative term is

$$\begin{aligned}
-\cos\theta\frac{a}{2}\frac{\partial^2}{\partial r^2}\left(\left(\frac{r^2}{2} + ar\right) e^{-r/a}\right) &= -\cos\theta\frac{a}{2}\frac{\partial}{\partial r}\left(\left((r+a) - \frac{1}{a}\left(\frac{r^2}{2} + ar\right)\right) e^{-r/a}\right) \\
&= -\cos\theta\frac{a}{2}\left(1 - \frac{2}{a}(r+a) + \frac{1}{a^2}\left(\frac{r^2}{2} + ar\right)\right) e^{-r/a} \\
&= \cos\theta\left(\frac{a}{2} + \frac{r}{2} - \frac{r^2}{4a}\right) e^{-r/a} \, .
\end{aligned}$$

The first derivative term is

$$\begin{aligned}
-\cos\theta\frac{a}{r}\frac{\partial}{\partial r}\left(\left(\frac{r^2}{2} + ar\right) e^{-r/a}\right) &= -\cos\theta\frac{a}{r}\left((r+a) - \frac{1}{a}\left(\frac{r^2}{2} + ar\right)\right) e^{-r/a} \\
&= \cos\theta\left(\frac{r}{2} - \frac{a^2}{r}\right) e^{-r/a} \, .
\end{aligned}$$

The angular derivative term is

$$\begin{aligned}
-\frac{a}{2r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right)\cos\theta\left(\frac{r^2}{2} + ar\right) e^{-r/a} &= \frac{a}{r^2}\cos\theta\left(\frac{r^2}{2} + ar\right) e^{-r/a} \\
&= \cos\theta\left(\frac{a}{2} + \frac{a^2}{r}\right) e^{-r/a} \, .
\end{aligned}$$

The potential term is

$$-\frac{e^2}{r}\left(\frac{ma}{\hbar^2}\left(\frac{r^2}{2}+ar\right)\cos\theta\, e^{-r/a}\right) = \cos\theta\left(-\frac{r}{2}-a\right)e^{-r/a}\ .$$

The first term on the right of equation (1) is considerably easier to evaluate,

$$\begin{aligned}
AH_0\,|0\rangle &= A\left(-\frac{e^2}{2a}\right)e^{-r/a} \\
&= \left(-\frac{e^2}{2a}\right)\left(-\frac{ma}{\hbar^2}\left(\frac{r^2}{2}+ar\right)\cos\theta\, e^{-r/a}\right) \\
&= \cos\theta\left(\frac{r^2}{4a}+\frac{r}{2}\right)e^{-r/a}\ .
\end{aligned}$$

We now add up the results of the last 5 calculations to find

$$\begin{aligned}
(AH_0 - H_0A)\,|0\rangle &= \cos\theta\left(\frac{a}{2}+\frac{r}{2}-\frac{r^2}{4a}+\frac{r}{2}-\frac{a^2}{r}+\frac{a}{2}+\frac{a^2}{r}-\frac{r}{2}-a+\frac{r^2}{4a}+\frac{r}{2}\right)e^{-r/a} \\
&= \cos\theta\, re^{-r/a} \\
&= z\,|0\rangle\ ,
\end{aligned}$$

which is what was to be shown!

End Solution

(c) Calculate the Stark effect energy shift for the ground state of hydrogen to second order in the applied field.

Solution

We need to evaluate $\langle 0 \mid zA \mid 0\rangle$. Here, the normalization of $|0\rangle$ matters, so we use $|0\rangle = 2(a)^{-3/2}(4\pi)^{-1/2}\exp(-r/a)$. Also, zA is proportional to z^2. As far as evaluating the matrix element, we can use symmetry to replace z^2 by $r^2/3$. So,

$$\begin{aligned}
e^2\,\langle 0 \mid zA \mid 0\rangle &= -\int_0^\infty \left(\frac{r}{2}+a\right)\frac{r^2}{3}\frac{4}{a^3}e^{-2r/a}r^2\,dr \\
&= -\frac{9}{4}a^3\ .
\end{aligned}$$

Finally, we need to include E^2 in the energy shift, so

$$\Delta E_1 = -\frac{9}{4}a^3E^2\ .$$

End Solution

2. A particle in a 2D box. (Based on a problem from Merzbacher.) A particle is confined to a square box, $0 \le x \le L$ and $0 \le y \le L$. We are not interested in the z-motion, so this is a 2D problem.

(a) Obtain the energies and eigenfunctions. What is the degeneracy of the few lowest levels?

Solution

The wave function must vanish at the boundaries of the box. This means

$$|nm\rangle = \frac{2}{L}\sin(n\pi x/L)\sin(m\pi y/L)\,,$$

where n and m are integers greater than 0. The energy is

$$E_{nm} = \frac{\hbar^2\pi^2}{2mL^2}\left(n^2+m^2\right)\,.$$

The degeneracy has to do with how many ways one can choose n and m to give the same n^2+m^2. The ground state is non-degenerate with $n=m=1$. The first excited state has a degeneracy of 2 with $n=2$, $m=1$ or $n=1$, $m=2$. The next excited state is non-degenerate with $n=m=2$. The third excited state is doubly degenerate with $n=3$, $m=1$ or $n=1$, $m=3$. That's enough!

End Solution

(b) A small perturbation $V = Cxy$, where C is a constant, is applied. Find the energy change for the ground state and the first excited state in the lowest non-vanishing order. Construct the appropriate eigenfunctions in the case of the first excited state.

Solution

We calculate

$$\begin{aligned}\int_0^L x\frac{2}{L}\sin\frac{n_1\pi x}{L}\sin\frac{n_2\pi x}{L}\,dx &= \frac{2L}{\pi^2}\int_0^\pi \sin n_1x\,\sin n_2x\,x\,dx\\ &= \frac{L}{\pi^2}\int_0^\pi \left(\cos((n_1-n_2)x)-\cos((n_1+n_2)x)\right)\,x\,dx\end{aligned}$$

The integrals can be evaluated with an integration by parts. If $n_1 \ne n_2$, the result is

$$\int_0^L x\frac{2}{L}\sin\frac{n_1\pi x}{L}\sin\frac{n_2\pi x}{L}\,dx = \frac{L}{\pi^2}\left(\frac{(-1)^{n_1-n_2}-1}{(n_1-n_2)^2}-\frac{(-1)^{n_1+n_2}-1}{(n_1+n_2)^2}\right)\,.$$

If n_1 and n_2 are both odd or both even, the result is 0. If one is odd and the other is even, the result is

$$\int_0^L x\frac{2}{L}\sin\frac{n_1\pi x}{L}\sin\frac{n_2\pi x}{L}\,dx = -\frac{8L}{\pi^2}\frac{n_1n_2}{(n_1^2-n_2^2)^2}\,.$$

If $n_1 = n_2$, the result is $L/2$.

So, the ground state changes energy by

$$\Delta E_{11} = \langle 11 \mid Cxy \mid 11 \rangle = CL^2/4\,,$$

since the expectation value is the product of two of the integrals just discussed with $n_1 = n_2 = m_1 = m_2 = 1$.

The first excited state is degenerate, so we need to choose a basis which diagonalizes the perturbation. We calculate the matrix elements for all the states:

$$\begin{pmatrix} \langle 21 \mid V \mid 21 \rangle & \langle 21 \mid V \mid 12 \rangle \\ \langle 12 \mid V \mid 21 \rangle & \langle 12 \mid V \mid 12 \rangle \end{pmatrix} = CL^2 \begin{pmatrix} 1/4 & 256/81\pi^4 \\ 256/81\pi^4 & 1/4 \end{pmatrix}\,.$$

The eigenvalues of this matrix are

$$\Delta E_{\text{first excited}} = CL^2 \left(\frac{1}{4} \pm \frac{256}{81\pi^4} \right)\,,$$

with eigenvectors

$$|\text{first excited}_\pm\rangle = \frac{1}{\sqrt{2}} \left(|21\rangle \pm |12\rangle \right)\,.$$

——————— End Solution ———————

3. Hyperfine splitting of the hydrogen ground state. As you know, the spatial part of the hydrogen ground state is very simple: $\psi_{100}(r, \theta, \phi) = \exp(-r/a)\, a^{(-3/2)}\, \pi^{(-1/2)}$. Since there is no orbital angular momentum, there is no spin orbit effect. However, the ground state has a degeneracy of 4 since both the proton and the electron have spin 1/2. The spins can align, giving a triplet state, or anti-align, giving a singlet state. Since there are magnets associated with the spins, we expect that there should be a difference in energy between the triplet and singlet states. The nuclear spin is often denoted by $\boldsymbol{I}$ and produces a magnetic moment

$$\boldsymbol{\mu}_p = \frac{eg_p}{2m_pc}\boldsymbol{I}\,,$$

where $\boldsymbol{\mu}_p$ is the magnetic moment of the proton, g_p is its g-factor and m_p is the mass of the proton. (Note: to consider other nuclei, we would use the appropriate Z, g, and m.) We take the proton as fixed at the origin and it produces a magnetic field,

$$\boldsymbol{B}(\boldsymbol{r}) = \frac{3\boldsymbol{e}_r(\boldsymbol{e}_r \cdot \boldsymbol{\mu}_p) - \boldsymbol{\mu}_p}{r^3} + \frac{8\pi}{3}\boldsymbol{\mu}_p \delta(\boldsymbol{r})\,,$$

(Jackson, *Classical Electrodynamics*, 2nd ed., p. 184). The interaction energy of this field and the magnetic moment of the electron is

$$H_{HF} = -\boldsymbol{\mu}_e \cdot \boldsymbol{B} = -\frac{3(\boldsymbol{e}_r \cdot \boldsymbol{\mu}_e)(\boldsymbol{e}_r \cdot \boldsymbol{\mu}_p) - \boldsymbol{\mu}_e \cdot \boldsymbol{\mu}_p}{r^3} - \frac{8\pi}{3}(\boldsymbol{\mu}_e \cdot \boldsymbol{\mu}_p)\delta(\boldsymbol{r})\,.$$

Aside: If we were to consider other than s-states, the hyperfine Hamiltonian would also include a spin orbit term due to the interaction of the magnetic moment of the nucleus with magnetic field produced by the moving electron(s).

Evaluate the hyperfine Hamiltonian above for the ground state of hydrogen. How does it depend on the proton and electron spins? Or, what is the energy difference between the singlet and triplet states? Which is the actual ground state: triplet or singlet? What are the wavelength and frequency of the radiation emitted or absorbed in the transition between these states? Hint: can you show that the first term in H_{HF} vanishes for s-states?

Solution

The first term in the hyperfine Hamiltonian is zero by the following argument. The numerator times r^2 is $3x_i\mu_{ei}x_j\mu_{pj} - r^2\boldsymbol{\mu}_e \cdot \boldsymbol{\mu}_p$. When we take the expectation value with an s-state, the angular integral will eliminate cross terms x_ix_j with $i \neq j$. The squared terms averaged over angles become $r^2/3$. This leaves $3\boldsymbol{\mu}_e \cdot \boldsymbol{\mu}_p\, r^2/3 - r^2\boldsymbol{\mu}_e \cdot \boldsymbol{\mu}_p = 0$.

The δ-function in the second term is a three dimensional delta function and it just picks out the value of the integrand at the origin. So,

$$\langle 100 \mid -8\pi\boldsymbol{\mu}_e \cdot \boldsymbol{\mu}_p/3 \mid 100\rangle = -8\boldsymbol{\mu}_e \cdot \boldsymbol{\mu}_p/3a^3\ .$$

The product of the magnetic moments is

$$\begin{aligned}\boldsymbol{\mu}_e \cdot \boldsymbol{\mu}_p &= \frac{-eg_e}{2m_ec}\frac{eg_p}{2m_pc}\boldsymbol{S}\cdot\boldsymbol{I} \\ &= -\frac{g_eg_p}{\hbar^2}\mu_B\mu_N\left[\frac{1}{2}\left(F^2 - S^2 - I^2\right)\right]\ ,\end{aligned}$$

where μ_B and μ_N are the Bohr and nuclear magnetons, and F is the total spin. $S^2 = I^2 = 3\hbar^2/4$. For the singlet state $F = 0$, $F^2 = 0$ and the quantity in brackets is $-3\hbar^2/4$. For a triplet state, $F = 1$, $F^2 = 2\hbar^2$. and the quantity in brackets is $+\hbar^2/4$.

Putting everything together, we wind up with

$$\begin{aligned}\langle H_{HFt}\rangle &= +\frac{2g_eg_p\mu_B\mu_N}{3a^3} \\ \langle H_{HFs}\rangle &= -\frac{2g_eg_p\mu_B\mu_N}{a^3} \\ \langle H_{HFt}\rangle - \langle H_{HFs}\rangle &= +\frac{8g_eg_p\mu_B\mu_N}{3a^3}\ .\end{aligned}$$

We see that the singlet is the ground state.

For the numerical evaluation, we use $g_e = 2$, $g_p = 5.59$, $\mu_B = 0.927 \times 10^{-20}\,\mathrm{erg\,G^{-1}}$, $\mu_N = 0.505 \times 10^{-23}\,\mathrm{erg\,G^{-1}}$, $a = 0.529 \times 10^{-8}\,\mathrm{cm}$. We find,

$$\begin{aligned}\Delta H_{HF} &= 9.43 \times 10^{-18}\,\mathrm{erg} = 5.89 \times 10^{-6}\,\mathrm{eV}\\ \nu_{HF} &= 1.42 \times 10^{9}\,\mathrm{Hz}\\ \lambda_{HF} &= 21\,\mathrm{cm}\,.\end{aligned}$$

This transition is the famous 21 cm line of neutral Hydrogen which is seen all over the sky. It's one of the principal ways to study our galaxy and other galaxies with radio telescopes!

End Solution

4. Zeeman splitting. We consider an atom with a single valence electron, subject to a magnetic field $\boldsymbol{B} = B\boldsymbol{e}_z$ in the z-direction. The Hamiltonian for the electron is

$$H = H_0 + H_{so} + H_B\,,$$

where

$$H_0 = \frac{P^2}{2m} + V(r)\,,$$

accounts for the dominant electric interaction of the electron (for Hydrogen, $V(r) = e^2/r$, for alkali metals, $V(r)$ takes account of the filled shells in an approximate way). The spin orbit interaction is

$$H_{so} = \frac{1}{2m^2c^2}\,\frac{1}{r}\,\frac{dV}{dr}\,\boldsymbol{L}\cdot\boldsymbol{S} = f(r)\,\boldsymbol{L}\cdot\boldsymbol{S}\,.$$

The interaction with the applied magnetic field is

$$H_B = \frac{eB}{2mc}(L_z + gS_z) = \frac{eB}{2mc}(L_z + 2S_z) = \frac{eB}{2mc}(J_z + S_z)\,,$$

where the term proportional to B^2 has been dropped. Also, some other small terms, for example, the relativistic correction to the momentum, have been dropped since they don't give a splitting dependent on j, l and s. In the calculations below, we are interested in H_{so} and H_B; H_0 determines the zeroth order energies and states which are used in computing expectation values of, for example, $f(r)$, but can otherwise be ignored.

(a) Suppose the magnetic field is very weak. What are the appropriate basis states and what are the spin-orbit and Zeeman splittings?

Solution

If the magnetic field is completely turned off, there is only the spin-orbit interaction. The appropriate states are those of total angular momentum, z-component of angular momentum, and orbital and spin angular momentum: $|njm_jls\rangle$. These states diagonalize the spin-orbit interaction which is assumed to be larger than the Zeeman interaction.

$$\langle H_{so}\rangle = \langle f(r)\rangle_{nl}\,\frac{\hbar^2}{2} \times \begin{cases} l & j = l + 1/2 \\ -(l+1) & j = l - 1/2 \end{cases}$$

Using these basis states we need to calculate the matrix elements of the Zeeman term,

$$\langle H_B \rangle = \left\langle njm_jls \,\middle|\, \frac{eB}{2mc}(J_z + S_z) \,\middle|\, njm_jls \right\rangle .$$

The matrix element of J_z is just $m_j\hbar$. The matrix element of S_z requires more work. In particular, the states $|njm_jls\rangle$ must be written in terms of $|nlm_l\rangle\,|sm_s\rangle$. Recall the expansions given in lecture,

$$\begin{aligned}
|j = l+1/2, m_j, l\rangle &= +\sqrt{\frac{l+m_j+1/2}{2l+1}}\,|lm_j - 1/2\rangle\,|\uparrow\rangle + \sqrt{\frac{l-m_j+1/2}{2l+1}}\,|lm_j + 1/2\rangle\,|\downarrow\rangle \\
|j = l-1/2, m_j, l\rangle &= -\sqrt{\frac{l-m_j+1/2}{2l+1}}\,|lm_j - 1/2\rangle\,|\uparrow\rangle + \sqrt{\frac{l+m_j+1/2}{2l+1}}\,|lm_j + 1/2\rangle\,|\downarrow\rangle .
\end{aligned}$$

With these expansions given in lecture, we find

$$\langle J_z + S_z \rangle = \frac{\hbar m_j}{2l+1} \times \begin{cases} 2l+2 & j = l+1/2 \\ 2l & j = l-1/2 \end{cases} .$$

Both cases are covered by

$$\langle J_z + S_z \rangle = \hbar m_j \frac{2j+1}{2l+1} = \hbar m_j g ,$$

where the g-factor varies from 2 for $l = 0$ to 1 for $l \to \infty$. Then the Zeeman term is

$$\langle H_B \rangle = g m_j \mu_B B .$$

Each spin-orbit level is split into $2j+1$ equi-spaced levels by the Zeeman effect.

——— End Solution ———

(b) Now suppose the magnetic field is very strong so the Zeeman term is larger than the spin-orbit term. What are the appropriate states and what are the Zeeman and spin-orbit splittings?

——— Solution ———

The Zeeman term is diagonal in the basis $|lm_l\rangle\,|m_s\rangle$ and

$$\langle H_B \rangle = \frac{eB}{2mc}\,\langle L_z + 2S_z \rangle = \frac{eB}{2mc}\hbar(m_l + 2m_s) = (m_l + 2m_s)\mu_B B .$$

In this basis, the spin-orbit term is easy to evaluate,

$$\langle \boldsymbol{L} \cdot \boldsymbol{S} \rangle = \langle L_x S_x + L_y S_y + L_z S_z \rangle = \langle L_z S_z \rangle = \hbar^2 m_l m_s .$$

Then

$$\langle H_{so} \rangle = m_l m_s \hbar^2 \langle f(r) \rangle_{nl} \; .$$

Note that in this limit there are some degeneracies. For example, if $l = 1$, then states $m_l = -1$, $m_s = +1/2$ and $m_l = +1$, $m_s = -1/2$ are degenerate.

End Solution

(c) Suppose that neither the spin-orbit nor the Zeeman effect is appreciably larger than the other. How would you determine the level splittings in this case? (This is a short essay question, no calculations are required!)

Solution

Pick a convenient basis for the levels that are degenerate in the absence of the spin-orbit and Zeeman interactions. Calculate the matrix elements in this basis. The eigenvalues of this matrix are the energy shifts in the states that correspond to the eigenvalues.

End Solution

5. Virial theorem for a particle in a fixed potential. (See Schwabl, chapter 12.) Consider $\boldsymbol{x} \cdot \boldsymbol{p}$ and a Hamiltonian $H = p^2/2m + V(\boldsymbol{x})$.

(a) Show that

$$[H, \boldsymbol{x} \cdot \boldsymbol{p}] = -i\hbar \left(\frac{p^2}{m} - \boldsymbol{x} \cdot \nabla V(\boldsymbol{x}) \right) \; .$$

Solution

We consider p^2 first:

$$\begin{aligned}
[p^2, \boldsymbol{x} \cdot \boldsymbol{p}] &= p_j p_j x_i p_i - x_i p_i p^2 \\
&= p_j (x_i p_j - i\hbar\delta_{ij}) p_i - x_i p_i p^2 \\
&= pj x_i p_j p_i - i\hbar p^2 - x_i p_i p^2 \\
&= (x_i p_j - i\hbar\delta_{ij}) p_j p_i - \hbar p^2 - x_i p_i p^2 \\
&= x_i p_i p^2 - 2i\hbar p^2 - x_i p_i p^2 \\
&= -2i\hbar p^2 \; .
\end{aligned}$$

Now $V(\boldsymbol{x})$:

$$\begin{aligned}
[V(\boldsymbol{x}), x_i p_i] &= V(\boldsymbol{x}) x_i p_i - x_i p_i V(\boldsymbol{x}) \\
&= V(\boldsymbol{x}) x_i p_i - x_i \left(\frac{\hbar}{i} \frac{\partial}{\partial x_i} V(\boldsymbol{x}) + V(\boldsymbol{x}) p_i \right) \\
&= +i\hbar \boldsymbol{x} \cdot \nabla V(\boldsymbol{x}) \; .
\end{aligned}$$

So,

$$[H, \boldsymbol{x} \cdot \boldsymbol{p}] = -i\hbar \left(\frac{p^2}{m} - \boldsymbol{x} \cdot \nabla V(\boldsymbol{x}) \right) \; .$$

——— End Solution ———

(b) If $|\psi\rangle$ is a stationary state of H, $H|\psi\rangle = E|\psi\rangle$, show that

$$\left\langle \psi \,\middle|\, \frac{p^2}{m} \,\middle|\, \psi \right\rangle - \langle \psi \mid \boldsymbol{x}\cdot\nabla V(\boldsymbol{x}) \mid \psi\rangle = 0\,,$$

and therefore, for the Coulomb potential,

$$2\langle \psi \mid H \mid \psi\rangle + \left\langle \psi \,\middle|\, \frac{Ze^2}{r} \,\middle|\, \psi \right\rangle = 0\,.$$

——— Solution ———

$$\begin{aligned}\langle \psi \mid [H, \boldsymbol{x}\cdot\boldsymbol{p}] \mid \psi\rangle &= \langle \psi \mid H\boldsymbol{x}\cdot\boldsymbol{p} - \boldsymbol{x}\cdot\boldsymbol{p}H \mid \psi\rangle \\ &= \langle \psi \mid E\boldsymbol{x}\cdot\boldsymbol{p} - \boldsymbol{x}\cdot\boldsymbol{p}E \mid \psi\rangle \\ &= E\langle \psi \mid \boldsymbol{x}\cdot\boldsymbol{p} - \boldsymbol{x}\cdot\boldsymbol{p} \mid \psi\rangle \\ &= 0\,.\end{aligned}$$

With the Coulomb potential, we have

$$\boldsymbol{x}\cdot\nabla\left(-\frac{Ze^2}{r}\right) = \boldsymbol{x}\cdot\left(+\frac{Ze^2\boldsymbol{x}}{r^3}\right) = +\frac{Ze^2}{r}\,.$$

So,

$$\begin{aligned}0 &= \left\langle \psi \,\middle|\, \frac{p^2}{m} \,\middle|\, \psi \right\rangle - \langle \psi \mid \boldsymbol{x}\cdot\nabla V(\boldsymbol{x}) \mid \psi\rangle \\ &= \left\langle \psi \,\middle|\, \frac{p^2}{m} \,\middle|\, \psi \right\rangle - \left\langle \psi \,\middle|\, \frac{Ze^2}{r} \,\middle|\, \psi \right\rangle \\ &= 2\left\langle \psi \,\middle|\, \frac{p^2}{2m} \,\middle|\, \psi \right\rangle - 2\left\langle \psi \,\middle|\, \frac{Ze^2}{r} \,\middle|\, \psi \right\rangle + \left\langle \psi \,\middle|\, \frac{Ze^2}{r} \,\middle|\, \psi \right\rangle \\ &= 2\langle \psi \mid H \mid \psi\rangle + \left\langle \psi \,\middle|\, \frac{Ze^2}{r} \,\middle|\, \psi \right\rangle\,.\end{aligned}$$

——— End Solution ———

(c) Determine $\langle 1/r\rangle_{nl}$ for the hydrogen atom.

——— Solution ———

From the above, we have

$$E_n = -\frac{1}{2}\left\langle \frac{Ze^2}{r} \right\rangle\,,$$

and we know, $E_n = -Z^2e^2/2an^2$, so

$$\left\langle \frac{1}{r} \right\rangle_{nl} = \frac{Z}{an^2}\,.$$

——— End Solution ———