Homework 3

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1

1.1

In order to keep the matrix elements invariant, in the Heisenberg picture we have

$$O_H = \mathrm{e}^{\mathrm{i}Ht/\hbar} O_S \mathrm{e}^{-\mathrm{i}Ht/\hbar}, \tag{1}$$

so that

$$_H\langle\psi'|O_H|\psi\rangle_H = {}_S\langle\psi'|O_S|\psi\rangle_S. \tag{2}$$

The differential time evolution equation is

$$\frac{\mathrm{d}O_H}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}HO_H - O_H \cdot \frac{\mathrm{i}}{\hbar}H + \mathrm{e}^{\mathrm{i}Ht/\hbar}\frac{\partial O_S}{\partial t}\mathrm{e}^{-\mathrm{i}Ht/\hbar}, \tag{3}$$

and therefore

$$
\begin{aligned}
\frac{\mathrm{d}\langle O\rangle}{\mathrm{d}t} &= \frac{1}{\mathrm{i}\hbar}\langle\psi_H|[O_H, H]|\psi_H\rangle + \langle\psi_H|\mathrm{e}^{\mathrm{i}Ht/\hbar}\frac{\partial O_S}{\partial t}\mathrm{e}^{-\mathrm{i}Ht/\hbar}|\psi_H\rangle \\
&= \frac{1}{\mathrm{i}\hbar}\langle\psi_H|[O_H, H]|\psi_H\rangle + \langle\psi_S|\frac{\partial O_S}{\partial t}|\psi_S\rangle \\
&= \frac{1}{\mathrm{i}\hbar}\langle[O, H]\rangle + \left\langle\frac{\partial O}{\partial t}\right\rangle.
\end{aligned} \tag{4}
$$

Note: here we assume H has no time dependence, and thus the time evolution operator assumes the simple form $\mathrm{e}^{-\mathrm{i}Ht/\hbar}$. The condition that H has no time dependence also means in the Heisenberg picture, $H_H(t) = H_H(0)$, and on the other hand, $H_H(t)$ can be obtained from $H_H(0)$ by replacing the values of all operators at $t = 0$ to the corresponding values at t, and therefore the commutation relation $[O_H(t), H]$ can be obtained by replacing the occurrences of all operators in $[O_H(t = 0), H] = [O_S, H]$ with their values at t. That's why in the third line, we omit the Heisenberg/Schrodinger picture labels.

1.2

Since the Hamiltonian

$$H = \frac{p^2}{2m} + V \tag{5}$$

is real (and not just Hermitian), we can always obtain real eigenfunctions. Thus

$$
\int \mathrm{d}x\, \psi^* x(-\mathrm{i}\hbar)\partial_x \psi = -\mathrm{i}\hbar\, \psi^* x\psi\Big|_{x=-\infty}^{\infty} + \mathrm{i}\hbar \int \mathrm{d}x\, \partial_x(\psi^* x)\psi
$$

$$
= \mathrm{i}\hbar \int \mathrm{d}x\, \partial_x(x\psi)\psi = \mathrm{i}\hbar \int \mathrm{d}x\, \psi^2 + \mathrm{i}\hbar \int \mathrm{d}x\, x(\partial_x\psi)\psi
$$

$$
= \mathrm{i}\hbar \int \mathrm{d}x\, |\psi|^2 - \int \mathrm{d}x\, \psi^* x(-\mathrm{i}\hbar\partial_x)\psi,
$$

and therefore

$$
2\int \mathrm{d}x\, \psi^* x p \psi = \mathrm{i}\hbar,
$$

$$
\langle xp\rangle = \mathrm{i}\hbar/2. \tag{6}
$$

Therefore

$$0 = \frac{\mathrm{d}}{\mathrm{d}t} \langle xp \rangle = \frac{1}{\mathrm{i}\hbar} \langle [xp, H] \rangle.$$

The commutation relation can be evaluated as (note the correspondence between Poisson brackets and commutators)

$$\begin{aligned}
[xp, H] &= \frac{1}{2m}[xp, p^2] + [xp, V(x)] \\
&= \frac{1}{2m}[x, p^2]\, p + x[p, V(x)] \\
&= \frac{1}{2m} \cdot 2\mathrm{i}\hbar p \cdot p - x \cdot \mathrm{i}\hbar \frac{\partial V(x)}{\partial x},
\end{aligned}$$

so we find

$$0 = \mathrm{i}\hbar \left\langle \frac{p^2}{m} \right\rangle - \mathrm{i}\hbar \left\langle x \frac{\partial V(x)}{\partial x} \right\rangle,$$

and therefore

$$2 \langle T \rangle = \left\langle x \frac{\partial V(x)}{\partial x} \right\rangle. \tag{7}$$

1.3

The proof can be repeated by replacing $x(-\mathrm{i}\hbar)\partial_x$ by $\boldsymbol{x} \cdot (-\mathrm{i}\hbar)\boldsymbol{\nabla}$. We then have

$$\begin{aligned}
\int \mathrm{d}^3\boldsymbol{x}\, \psi^* \boldsymbol{x} \cdot (-\mathrm{i}\hbar)\boldsymbol{\nabla}\psi &= -\mathrm{i}\hbar \oint \mathrm{d}\boldsymbol{S} \cdot (\psi^* \boldsymbol{x}\psi) + \mathrm{i}\hbar \int \mathrm{d}^3\boldsymbol{x}\, \boldsymbol{\nabla} \cdot (\psi^* \boldsymbol{x})\psi \\
&= \mathrm{i}\hbar \int \mathrm{d}^3\boldsymbol{x}\, \boldsymbol{\nabla} \cdot (\psi \boldsymbol{x})\psi \\
&= \mathrm{i}\hbar \int \mathrm{d}^3\boldsymbol{x}\, \psi^2 \underbrace{\boldsymbol{\nabla} \cdot \boldsymbol{x}}_{3} + \mathrm{i}\hbar \int \mathrm{d}^3\boldsymbol{x}\, \psi \boldsymbol{x} \cdot \boldsymbol{\nabla}\psi,
\end{aligned}$$

and we find

$$2 \langle \boldsymbol{x} \cdot \boldsymbol{p} \rangle = 3\mathrm{i}\hbar. \tag{8}$$

Then repeating the derivation above, we get

$$2 \langle T \rangle = \left\langle \boldsymbol{x} \cdot \frac{\partial V(\boldsymbol{x})}{\partial \boldsymbol{x}} \right\rangle. \tag{9}$$

1.4

When $V = -1/r$, we have

$$E = \langle V \rangle + \frac{1}{2} \left\langle r \frac{\partial V}{\partial r} \right\rangle = -\left\langle \frac{1}{r} \right\rangle + \frac{1}{2} \left\langle r \cdot \frac{1}{r^2} \right\rangle = -\frac{1}{2} \left\langle \frac{1}{r} \right\rangle < 0, \tag{10}$$

and therefore bound states are possible. When $V = -1/r^2$, however, we have

$$E = \langle V \rangle + \frac{1}{2} \left\langle r \frac{\partial V}{\partial r} \right\rangle = -\left\langle \frac{1}{r^2} \right\rangle + \frac{1}{2} \left\langle r \cdot \frac{2}{r^3} \right\rangle = 0, \tag{11}$$

which causes a contradiction: if a bound state exists, then its energy is not below $E = 0$. Thus the potential $V(r) = -1/r^2$ doesn't assume bound states.

2

We want to calculate

$$P_{\mathrm{stay}} = |\langle \mathrm{old\ ground}|U|\mathrm{new\ ground}\rangle|^2. \tag{12}$$

If the Hamiltonian of a system undergoes a sudden change at $t = 0$ and assumes now time evolution beside this point, the time evolution operator $U(t, 0)$ is trivial both when $t > 0$ and $t < 0$, and the probability is

$$P_{\mathrm{say}} = |\langle \mathrm{old\ ground}|\mathrm{new\ ground}\rangle|^2. \tag{13}$$

Now suppose ψ_0 is the 1s orbital of the electron in a hydrogen atom. The hydrogen atom obtains a momentum $-k\hat{z}$ after scattering with an α particle. In the frame of reference attached to the hydrogen atom after scattering, the old ground state is moving with momentum $k\hat{z}$, and its wave function therefore should be

$$\psi_{k0}(\boldsymbol{r}) = \mathrm{e}^{\mathrm{i}kz}\psi_0(\boldsymbol{r}). \tag{14}$$

The possibility for the electron to say at the ground state after the collision – in other words, the possibility for the electron to go from the old ground state to the new ground state – is therefore

$$P_{\mathrm{say}} = |\langle\psi_0|\psi_{k0}\rangle|^2 = \left|\int \mathrm{d}^3\boldsymbol{r}\,\mathrm{e}^{\mathrm{i}kz}|\psi_0(\boldsymbol{r})|^2\right|^2. \tag{15}$$

3

The two angular momentum degrees of freedom are the electron spin $\boldsymbol{S}$ and the nucleus spin $\boldsymbol{I}$. Since we are at $n = 0$, the electron has no orbital angular momentum. The magnetic coupling Hamiltonian is

$$H_{\mathrm{magnetic\ coupling}} = -\boldsymbol{\mu}\cdot\boldsymbol{B} = \frac{1}{\hbar}(2\mu_{\mathrm{B}}\boldsymbol{S} - g_p\mu_{\mathrm{N}}\boldsymbol{I})\cdot\boldsymbol{B}. \tag{16}$$

Considering the component of $\boldsymbol{\mu}$ along $\boldsymbol{F} = \boldsymbol{S} + \boldsymbol{I}$ only, we have

$$H_{\mathrm{magnetic\ coupling}} = \frac{1}{\hbar}\frac{(2\mu_{\mathrm{B}}\boldsymbol{S} - g_p\mu_{\mathrm{N}}\boldsymbol{I})\cdot(\boldsymbol{S} + \boldsymbol{I})}{\boldsymbol{F}^2}\boldsymbol{F}\cdot\boldsymbol{B}. \tag{17}$$

Expanding $\boldsymbol{S}^2, \boldsymbol{I}^2$ and $\boldsymbol{S}\cdot\boldsymbol{I}$, we have

$$\frac{E}{m_F B} = \frac{1}{\hbar}\frac{2\mu_{\mathrm{B}}S(S+1) - g_p\mu_{\mathrm{N}}I(I+1) + (2\mu_{\mathrm{B}} - g_p\mu_{\mathrm{N}})\cdot\frac{1}{2}(F(F+1) - S(S+1) - I(I+1))}{F(F+1)}. \tag{18}$$

Since we are working with hydrogen, $I = 1/2$, $S = 1/2$, and $F = 0, 1$, and therefore

$$E = \frac{1}{\hbar}\frac{2\mu_{\mathrm{B}} - g_p\mu_{\mathrm{N}}}{2}m_F B. \tag{19}$$

So we have

$$E_{F=1,m_F} = E_0 + E_g + \frac{2\mu_{\mathrm{B}} - g_p\mu_{\mathrm{N}}}{2\hbar}m_F B, \tag{20}$$

and

$$E_{F=0,m_F=0} = E_0, \tag{21}$$

where $E_0 = 13.6\,\mathrm{eV}$.

4

4.1

When the electric field $\boldsymbol{E}$ is along the z axis, the dipole interaction matrix is

$$H = -er\mathcal{E}\cos\theta. \tag{22}$$

When the initial state is

$$\psi_0(\boldsymbol{r}) = \frac{1}{\sqrt{\pi}}\mathrm{e}^{-r}, \tag{23}$$

the first-order energy correction is

$$E_0^{(1)} \propto \int \mathrm{d}\Omega\, r^2\,\mathrm{d}r\,\mathrm{e}^{-2r}r \propto \int_0^\infty r^3\mathrm{e}^{-2r} = 0 \tag{24}$$

by integration by parts.

4.2

We have (note that $\psi_0(\boldsymbol{r})$ has no θ or φ dependence)

$$
\begin{aligned}
\langle nlm|e\boldsymbol{r}\cdot\boldsymbol{E}|0\rangle &\propto \int \mathrm{d}^3\boldsymbol{r}\,\psi^*_{nlm}(\boldsymbol{r})r\cos\theta\psi_0(\boldsymbol{r}) \\
&\propto \int_0^\pi \sin\theta\,\mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\varphi\,\mathrm{e}^{-\mathrm{i}m\varphi}\,\mathrm{P}_l^{|m|}(\cos\theta)\cos\theta.
\end{aligned} \tag{25}
$$

The radial part always has a non-zero contribution, since the r factor is not in the $\{R_{nl}\}$ basis and therefore

$$
\int_0^\infty r^2\,\mathrm{d}r\,R_{00}(r)^* r R_{nl}(r)
$$

doesn't vanish because the orthogonal conditions are not available here. So in order to know when the transition is not possible, we only need to focus on the θ and φ parts. For the φ part

$$
\int_0^{2\pi}\mathrm{e}^{-\mathrm{i}m\varphi}\,\mathrm{d}\varphi
$$

obviously vanishes except when $m=0$. When $m=0$, the θ part is

$$
\int_0^\pi \sin\theta\,\mathrm{d}\theta\,\mathrm{P}_l^{|m|}(\cos\theta)\cos\theta = \int_{-1}^1 x\,\mathrm{P}_l(x)\,\mathrm{d}x\,,
$$

and since $\mathrm{P}_1(x)=x$, due to orthogonal relations, only when $l=1$, the above expression has a non-zero value. Thus if a static electric field is added along the z axis, the only possible final state is $\psi_{n=1,m=0}$.

4.3

We want to use the Dalgarno-Lewis method and solve

$$
\left(H_0-E_n^{(0)}\right)\left|n^{(1)}\right\rangle = -\left(H'-E_n^{(1)}\right)\left|n^{(0)}\right\rangle,\quad E_n^{(2)}=\left\langle n^{(0)}\,|H'|\,n^{(1)}\right\rangle - E_n^{(1)}\left\langle n^{(0)}\mid n^{(0)}\right\rangle \tag{26}
$$

for the hydrogen ground state, where H' is given by (22). Since we work in the Hartree atomic units, we can set $e=-1$, and ground state energy is

$$
E_0^{(0)} = -\frac{1}{2}. \tag{27}
$$

Therefore the PDE about $\psi_0^{(1)}$ is

$$
\left(-\frac{\nabla^2}{2}-\frac{1}{r}+\frac{1}{2}\right)\psi_0^{(1)} = -r\mathcal{E}\cos\theta\psi^{(0)}(r) = -r\mathcal{E}\cos\theta\frac{1}{\sqrt{\pi}}\mathrm{e}^{-r}. \tag{28}
$$

Taking the ansatz

$$
\psi_0^{(1)}(\boldsymbol{r}) = (A+Br+Cr^2)\mathrm{e}^{-r}\cos\theta, \tag{29}
$$

we have

$$
\mathrm{LHS} = \mathrm{e}^{-r}\cos\theta\frac{A+(B-2C)r^2+2Cr^3}{r^2}.
$$

Comparing this with the RHS, we find

$$
A=0,\quad B-2C=0,\quad 2C=-\mathcal{E}\frac{1}{\sqrt{\pi}},
$$

and therefore

$$
\psi_0^{(1)}(\boldsymbol{r}) = -\frac{\mathcal{E}}{2\sqrt{\pi}}(r^2+2r)\mathrm{e}^{-r}\cos\theta. \tag{30}
$$

Since $E_n^{(1)}$ vanishes, the second-order perturbation of the energy is

$$
\begin{aligned}
E_0^{(2)} &= \int \mathrm{d}^3 \boldsymbol{r} \, \frac{1}{\sqrt{\pi}} \mathrm{e}^{-r} \cdot (r\mathcal{E} \cos\theta) \cdot \frac{-\mathcal{E}}{2\sqrt{\pi}} (r^2 + 2r)\mathrm{e}^{-r} \cos\theta \\
&= -\frac{\mathcal{E}^2}{2\pi} \cdot 2\pi \cdot \int_0^\infty r^2 \, \mathrm{d}r \, (r^2 + 2r)\mathrm{e}^{-2r} \cdot \int_0^\pi \sin\theta \, \mathrm{d}\theta \cos^2\theta \qquad (31) \\
&= -\frac{\mathcal{E}^2}{2\pi} \cdot 2\pi \cdot \frac{3}{2} \cdot \frac{2}{3} = -\mathcal{E}^2 .
\end{aligned}
$$

This expression is a specific case of

$$
E^{(2)} = -\frac{1}{2}\alpha_{\mathrm{p}}\mathcal{E}^2 . \qquad (32)
$$

The expression can be shown by the following argument: due to selection rules (generalization of last section) for any atomic orbital, $E_n^{(1)} = 0$, and therefore

$$
E^{(2)} = \langle nlm^{(0)} | r\mathcal{E} \cos\theta | nlm^{(1)} \rangle , \qquad (33)
$$

while we have

$$
d = \langle nlm | -er\cos\theta | nlm \rangle \approx (\langle nlm^{(0)}| + \langle nlm^{(1)}|)(-er\cos\theta)(|nlm^{(0)}\rangle + |nlm^{(1)}\rangle) =: \alpha_{\mathrm{p}}\mathcal{E} . \quad (34)
$$

Ignoring the second order terms, and employing the condition that the eigenfunctions are all real, we find

$$
\langle nlm^{(0)} | r\cos\theta | nlm^{(1)} \rangle = -\alpha_{\mathrm{p}}\mathcal{E} ,
$$

and thus (32).