Physics 4410

Quantium Mechanics and Atomic Physics II

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Homework #7

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1 Problem #1

For the Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + \lambda x^4$$

we can apply *Variational Principle* to estimate the ground state energy. Variational principle states that the ground state energy has an upper bound that is set by

$$E_0 \leq \langle\psi|\hat{H}|\psi\rangle \tag{1.1}$$

where $|\psi\rangle$ is a trial wavefunction. We can pick $|\psi\rangle$ as a Gaussian of the form

$$|\psi(\alpha)\rangle = Ne^{-\alpha x^2/2}$$

where α is the varied parameter and N is the normalization factor which we calculate as

$$\begin{aligned}
1 = \int_{-\infty}^{\infty} \langle\psi(\alpha)|\psi(\alpha)\rangle &= N^2 \int_{-\infty}^{\infty} e^{-\alpha x^2} \\
&= N^2 \left(\frac{\pi}{\alpha}\right)^{1/2} \\
&\Downarrow \\
N &= \left(\frac{\alpha}{\pi}\right)^{1/4}
\end{aligned}$$

So now we can set an upper bound on the ground state energy by equation **??**

$$\begin{aligned}
E(\alpha) = \langle\psi|\hat{H}|\psi\rangle &= \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} dx e^{-\alpha x^2/2} \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \lambda x^4\right) e^{-\alpha x^2/2} \\
&= \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} dx e^{-\alpha x^2/2} \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} e^{-\alpha x^2/2} + \lambda x^4 e^{-\alpha x^2/2}\right) \\
&= \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} dx e^{-\alpha x^2/2} \left(\frac{\hbar^2}{2m}\frac{\partial}{\partial x}(\alpha x) e^{-\alpha x^2/2} + \lambda x^4 e^{-\alpha x^2/2}\right) \\
&= \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} dx e^{-\alpha x^2/2} \left(\frac{\hbar^2}{2m}\alpha e^{-\alpha x^2/2} - \frac{\hbar^2}{2m}(\alpha x)^2 e^{-\alpha x^2/2} + \lambda x^4 e^{-\alpha x^2/2}\right) \\
&= \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} dx e^{-\alpha x^2} \left(\frac{\hbar^2\alpha}{2m} - \frac{\hbar^2\alpha^2}{2m}x^2 + \lambda x^4\right)
\end{aligned}$$

Now we have three integrals involving the Gaussian $e^{-\alpha x^2}$. This allows us to use the fact that for even powers of x we have

$$\left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^{2n} e^{-\alpha x^2} = \left(\frac{1}{2\alpha}\right)^n (2n-1)!! \tag{1.2}$$

Note that $n!! = n(n-2)(n-4)....$ Note for x^2 we have $n = 1$ and for x^4 we have $n = 2$ so equation **??** yields

$$\begin{aligned}
\left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} &= \frac{1}{2\alpha} \\
\left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} &= \frac{3}{4\alpha^2}
\end{aligned}$$

Note the integral with the constant $\hbar^2\alpha/2m$ is just the constant due to normalization. So the integral becomes

$$\begin{aligned}
E(\alpha) &= \frac{\hbar^2\alpha}{2m} - \frac{\hbar^2\alpha^2}{2m}\frac{1}{2\alpha} + \lambda\frac{3}{4\alpha^2} \\
&= \frac{\hbar^2\alpha}{2m} - \frac{\hbar^2\alpha}{4m} + \lambda\frac{3}{4\alpha^2} \\
&= \frac{\hbar^2}{4m}\alpha + \lambda\frac{3}{4\alpha^2}
\end{aligned}$$

Now we just need to find α_0 that minimizes $E(\alpha)$ by

$$\begin{gathered}
0 = \frac{dE(\alpha)}{d\alpha} = \frac{\hbar^2}{4m} - \lambda\frac{3}{2\alpha_0^3} \\
\Downarrow \\
\frac{\hbar^2}{4m} = \lambda\frac{3}{2\alpha_0^3} \\
\Downarrow
\end{gathered}$$

$$\begin{aligned}
\alpha_0^3 &= \frac{3\lambda}{2}\frac{4m}{\hbar^2} \\
\alpha_0 &= \left(\frac{6m\lambda}{\hbar^2}\right)^{1/3}
\end{aligned}$$

Now we replace we can find $E(\alpha_0)$ by

$$\begin{aligned}
E(\alpha_0) &= \frac{\hbar^2}{4m}\alpha_0 + \lambda\frac{3}{4\alpha_0^2} \\
&= \frac{\hbar^2}{4m}\left(\frac{6m\lambda}{\hbar^2}\right)^{1/3} + \lambda\frac{3}{4}\left(\frac{6m\lambda}{\hbar^2}\right)^{-2/3} \\
&= \lambda^{1/3}\left(\frac{3\hbar^4}{32m^2}\right)^{1/3} + \lambda^{1/3}\frac{3}{4}\left(\frac{\hbar^2}{6m}\right)^{2/3} \\
&= \left(\frac{3}{8}\right)^{1/3}\lambda^{1/3}\left(\frac{\hbar^2}{2m}\right)^{2/3} + \frac{3}{4}\left(\frac{1}{3}\right)^{2/3}\lambda^{1/3}\left(\frac{\hbar^2}{2m}\right)^{2/3} \\
&= \left[\left(\frac{3}{8}\right)^{1/3} + \frac{3}{4}\left(\frac{1}{3}\right)^{2/3}\right]\lambda^{1/3}\left(\frac{\hbar^2}{2m}\right)^{2/3} \\
E_0 &\leq (1.081)\lambda^{1/3}\left(\frac{\hbar^2}{2m}\right)^{2/3}
\end{aligned}$$

Note that this is a accurate upper bound to the actual ground state energy given by

$$E_0 = (1.060)\lambda^{1/3}\left(\frac{\hbar^2}{2m}\right)^{2/3}$$

2 Problem #2

The H^+ ion problem reduces to the calculation of two integrals. The *direct integral*

$$D \equiv a\langle\psi_0(r_1)|\frac{1}{r_2}|\psi_0(r_1)\rangle$$

and the *exchange integral*

$$X \equiv a\langle\psi_0(r_1)|\frac{1}{r_1}|\psi_0(r_2)\rangle$$

where $|\psi_0(r)\rangle$ is the ground state wavefunction of the hydrogen atom given by

$$|\psi_0(r)\rangle = \frac{1}{\sqrt{\pi a^3}}e^{-r/a}$$

Note that the *Law of Cosines* relates r_1 with r_2 by picking a proton as the origin such that

$$\begin{aligned} r_1 &\to r \\ r_2 &\to |\vec{r} - \vec{R}| = \sqrt{r^2 + R^2 - 2rR\cos(\theta)} \end{aligned}$$

Where R is the separation between the two protons. So we can calculate D by

$$\begin{aligned} D \equiv a\langle\psi_0(r_1)|\frac{1}{r_2}|\psi_0(r_1)\rangle = a\langle\psi_0(r_2)|\frac{1}{r_1}|\psi_0(r_2)\rangle \\ &= \frac{a}{\pi a^3}\int_0^\infty\int_0^\pi\int_0^{2\pi} e^{-2\sqrt{r^2+R^2-2rR\cos(\theta)}/a}\frac{1}{r}r^2\sin(\theta)drd\theta d\phi \\ &= \frac{2\pi}{\pi a^2}\int_0^\infty\int_0^\pi e^{-2\sqrt{r^2+R^2-2rR\cos(\theta)}/a}r\sin(\theta)drd\theta \end{aligned}$$

Note we can solve the θ integral by a substitution where

$$\begin{aligned} u &= \sqrt{r^2 + R^2 - 2rR\cos(\theta)} \\ du &= \frac{1}{2}(r^2 + R^2 - 2rR\cos(\theta))^{-1/2}2rR\sin(\theta)d\theta \\ &\Downarrow \\ \frac{u}{rR}du &= \sin(\theta)d\theta \end{aligned}$$

Note that the bounds of integration become

$$\begin{aligned} u(0) &= \sqrt{r^2 + R^2 - 2rR\cos(0)} = \sqrt{r^2 + R^2 - 2rR} = \sqrt{(r-R)^2} = |r - R| \\ u(\pi) &= \sqrt{r^2 + R^2 - 2rR\cos(\pi)} = \sqrt{r^2 + R^2 + 2rR} = \sqrt{(r+R)^2} = |r + R| \end{aligned}$$

Which gives

$$\begin{aligned} \int_0^\pi e^{-2\sqrt{r^2+R^2-2rR\cos(\theta)}/a}\sin(\theta)d\theta &= \frac{1}{rR}\int_{u(0)}^{u(\pi)} e^{-2u/a}udu \\ &= \frac{1}{rR}\int_{|r-R|}^{r+R} e^{-2u/a}udu \\ &= \frac{1}{rR}\left(-\frac{1}{4}ae^{-2u/a}(a + 2u)\right|_{|r-R|}^{r+R} \\ &= -\frac{a}{2rR}\left(e^{-2(r+R)/a}(a/2 + r + R) - e^{-2(r-R)/a}(a/2 + r - R)\right) \end{aligned}$$

So now we can solve for D

$$\begin{aligned} D &= \frac{2}{a^2}\frac{a}{2R}\int_0^\infty\left(e^{-2(r+R)/a}(a/2 + r + R) - e^{-2|r-R|/a}(a/2 + |r - R|)\right)\frac{1}{r}rdr \\ &= -\frac{1}{aR}\int_0^\infty\left(e^{-2(r+R)/a}(a/2 + r + R) - e^{-2|r-R|/a}(a/2 + |r - R|)\right)dr \\ &= -\frac{1}{aR}\left(e^{-2R/a}\int_0^\infty e^{-2r/a}(a/2 + r + R)dr - \int_0^\infty e^{-2|r-R|/a}(a/2 + |r - R|)dr\right) \end{aligned}$$

Note we can calculate the first integral over all r by

$$\int_0^\infty e^{-2r/a}(a/2 + r + R)dr = \frac{a^2 + aR}{2}$$

But due to the absolute value we must break the bounds for the second term such that

$$\begin{aligned}
\int_0^\infty e^{-2|r-R|/a}(a/2 + |r - R|)dr &= \int_0^R e^{-2(R-r)/a}(a/2 + R - r)dr + \int_R^\infty e^{-2(r-R)/a}(a/2 + r - R)dr \\
&= e^{-2R/a}\int_0^R e^{2r/a}(a/2 + R - r)dr + e^{2R/a}\int_R^\infty e^{-2r/a}(a/2 + r - R)dr \\
&= e^{-2R/a}\left(\frac{1}{2}a(a(e^{2R/a} - 1) - R)\right) + \frac{a^2}{2} \\
&= \frac{a^2}{2} - \frac{a^2}{2}e^{-2R/a} - \frac{aR}{2}e^{-2R/a} + \frac{a^2}{2} \\
&= a^2 - \frac{a^2}{2}e^{-2R/a} - \frac{aR}{2}e^{-2R/a}
\end{aligned}$$

So brining it all together we get

$$\begin{aligned}
D &= -\frac{1}{aR}\left(\frac{a^2}{2}e^{-2R/a} + \frac{aR}{2}e^{-2R/a} - a^2 + \frac{a^2}{2}e^{-2R/a} + \frac{aR}{2}e^{-2R/a}\right) \\
&= -\frac{a^2}{2aR}e^{-2R/a} - \frac{aR}{2aR}e^{-2R/a} + \frac{a^2}{aR} - \frac{a^2}{2aR}e^{-2R/a} - \frac{aR}{2aR}e^{-2R/a} \\
&= -\frac{a}{2R}e^{-2R/a} - \frac{1}{2}e^{-2R/a} + \frac{a}{R} - \frac{a}{2R}e^{-2R/a} - \frac{1}{2}e^{-2R/a} \\
&= \frac{a}{R} - \left(\frac{a}{2R} + \frac{1}{2} + \frac{a}{2R} + \frac{1}{2}\right)e^{-2R/a} \\
&= \frac{a}{R} - \left(1 + \frac{a}{R}\right)e^{-2R/a}
\end{aligned}$$

And now we can calculate X by

$$\begin{aligned}
X \equiv a\langle\psi_0(r_1)|\frac{1}{r_1}|\psi_0(r_2)\rangle &= \frac{a}{\pi a^3}\int_0^\infty\int_0^\pi\int_0^{2\pi} e^{-r/a}e^{-\sqrt{r^2+R^2-2rR\cos(\theta)}/a}\frac{1}{r}r^2\sin(\theta)drd\theta d\phi \\
&= \frac{2}{a^2}\int_0^\infty re^{-r/a}dr\int_0^\pi e^{-\sqrt{r^2+R^2-2rR\cos(\theta)}/a}\sin(\theta)d\theta \\
&= \frac{2}{a^2}\int_0^\infty re^{-r/a}dr\left(-\frac{a}{rR}\left(e^{-(r+R)/a}(a + r + R) - e^{-|r-R|/a}(a + |r - R|)\right)\right)
\end{aligned}$$

Note we solved the θ integral with an extra factor of 2 already. This leaves the r integral

$$\begin{aligned}
X &= -\frac{2}{aR}\int_0^\infty e^{-r/a}\left(e^{-(r+R)/a}(a + r + R) - e^{-|r-R|/a}(a + |r - R|)\right)dr \\
&= -\frac{2}{aR}\left(e^{-R/a}\int_0^\infty e^{-2r/a}(a + r + R)dr - \int_0^\infty e^{-r/a}e^{-|r-R|/a}(a + |r - R|)dr\right)
\end{aligned}$$

Again the first integral can be done over all r

$$e^{-R/a}\int_0^\infty e^{-2r/a}(a + r + R)dr = \frac{3a^2}{4}e^{-R/a} + \frac{aR}{2}e^{-R/a}$$

and the second integral is split such that

$$\begin{aligned}
\int_0^\infty e^{-r/a}e^{-|r-R|/a}(a+|r-R|)dr &= \int_0^R e^{-r/a}e^{-(R-r)/a}(a+R-r)dr + \int_R^\infty e^{-r/a}e^{-(r-R)/a}(a+r-R)dr \\
&= e^{-R/a}\int_0^R e^{-r/a}e^{r/a}(a+R-r)dr + e^{R/a}\int_R^\infty e^{-r/a}e^{-r/a}(a+r-R)dr \\
&= e^{-R/a}\int_0^R (a+R-r)dr + e^{R/a}\int_R^\infty e^{-2r/a}(a+r-R)dr \\
&= e^{-R/a}\left(aR+\frac{R^2}{2}\right) + \frac{3a^2}{4}e^{-R/a} \\
&= e^{-R/a}\left(aR+\frac{R^2}{2}+\frac{3a^2}{4}\right)
\end{aligned}$$

Putting it all together yields

$$\begin{aligned}
X &= -\frac{2}{aR}\left(\frac{3a^2}{4}e^{-R/a} + \frac{aR}{2}e^{-R/a} - e^{-R/a}\left(aR+\frac{R^2}{2}+\frac{3a^2}{4}\right)\right) \\
&= -\frac{2}{aR}\left(\frac{3a^2}{4}+\frac{aR}{2}-aR-\frac{R^2}{2}-\frac{3a^2}{4}\right)e^{-R/a} \\
&= 2\left(-\frac{aR}{2aR}+\frac{aR}{aR}-\frac{R^2}{2aR}\right)e^{-R/a} \\
&= 2\left(\frac{1}{2}-\frac{R}{2a}\right)e^{-R/a} \\
&= \left(1-\frac{R}{a}\right)e^{-R/a}
\end{aligned}$$

3 Problem #3

For a time dependent electric field

$$E(t) = E_0 e^{-\gamma t}$$

which points in the $\hat{z}$ direction we have the time dependent potential

$$V(r,\theta,t) = E_0 e^{-\gamma t} r\cos(\theta)$$

Using *Time-Dependent Perturbation Theory* we can calculate the coefficient c_f that corresponds to the transition from an initial state $|i\rangle$ to a final state $|f\rangle$ by

$$c_f(t) = -\frac{i}{\hbar}\int_0^t \langle f|V(\mathbf{r},t')|i\rangle e^{\frac{i}{\hbar}(E_f-E_i)t'}dt' \tag{3.1}$$

Now we assuming that we are initially in the ground state of hydrogen ($|100\rangle$) and we want to transition to the $2p$ state represented by $|21m\rangle$. Note that there is a degeneracy at this level but we note that the potential goes by $\cos(\theta)$ and the ground state has no θ dependence. This implies that the final state must be an even function for the matrix element $\langle f|V|i\rangle$ to be non-zero. The only state that satisfies this requirement is the $|210\rangle$ state as it also goes by $\cos(\theta)$. Note the $|21\pm1\rangle$ states go by $\sin(\theta)$ which is why they go to zero. So we can calculate equation **??** by

$$\begin{aligned}
c_f(t) &= -\frac{i}{\hbar}\int_0^t \langle 210|E_0 r\cos(\theta)e^{-\gamma t'}|100\rangle e^{\frac{i}{\hbar}(E_f-E_i)t'}dt' \\
&= -E_0\frac{i}{\hbar}\int_0^t \langle 210|r\cos(\theta)|100\rangle e^{-\gamma t'}e^{\frac{i}{\hbar}(E_f-E_i)t'}dt'
\end{aligned}$$

Now we need to calculate

$$\begin{aligned}
\langle 210|r\cos(\theta)|100\rangle &= \left(\frac{3}{4\pi}\frac{1}{4\pi}\right)^{1/2}\left(\frac{1}{24a^3}\frac{2}{a^3}\right)^{1/2} a\int_0^\infty\int_0^\pi\int_0^{2\pi} r^{-r/2a}\cos(\theta)r\cos(\theta)e^{-r/a}r^2\sin(\theta)drd\theta d\phi \\
&= \frac{2\pi}{8\pi a^2}\int_0^\infty r^{-r/2a}r^3e^{-r/a}dr\int_0^\pi \cos^2(\theta)\sin(\theta)d\theta \\
&= \frac{1}{4a^2}\frac{2}{3}\int_0^\infty r^{-r/2a}r^3e^{-r/a}dr \\
&= \frac{1}{6a^2}\frac{96a^4}{(2+a^2)^4} = \frac{16a^2}{(2+a^2)^4}
\end{aligned}$$

Now replacing this result in equation **??** we get

$$c_f(t) = -E_0\frac{i}{\hbar}\frac{16a^2}{(2+a^2)^4}\int_0^t e^{-\gamma t'}e^{\frac{i}{\hbar}(E_f-E_i)t'}dt'$$

Now we can calculate the probability of this transition happening by finding $|c_f(t)|^2$ by

$$\begin{aligned}
|c_f(t)|^2 &= \left(\frac{E_0}{\hbar}\frac{16a^2}{(2+a^2)^4}\right)^2\int_0^t e^{-\gamma t'}e^{-\frac{i}{\hbar}(E_f-E_i)t'}e^{-\gamma t'}e^{\frac{i}{\hbar}(E_f-E_i)t'}dt' \\
&= \left(\frac{E_0}{\hbar}\frac{16a^2}{(2+a^2)^4}\right)^2\int_0^t e^{-2\gamma t'}dt' \\
&= -\left(\frac{E_0}{\hbar}\frac{16a^2}{(2+a^2)^4}\right)^2\frac{e^{-2\gamma t}-1}{2\gamma}
\end{aligned}$$

Now we can take $t\to\infty$ and find that

$$\begin{aligned}
\lim_{t\to\infty}|c_f(t)|^2 &= \lim_{t\to\infty} -\left(\frac{E_0}{\hbar}\frac{16a^2}{(2+a^2)^4}\right)^2\frac{\cancelto{0}{e^{-2\gamma t}}-1}{2\gamma} \\
&= \left(\frac{E_0}{\hbar}\frac{16a^2}{(2+a^2)^4}\right)^2\frac{1}{2\gamma}
\end{aligned}$$