1. More H atom expectation values. For the relativistic corrections with the Coulomb potential, we needed to know $\left\langle 1/r^2 \right\rangle$ and $\left\langle 1/r^3 \right\rangle$. These can be calculated from the radial wave functions, but there is an easier way. We start with radial wave functions $u(r) = rR(r)$ and rewrite the radial Schroedinger equation in the dimensionless variable $y = r/a$.

(a) Show that the resulting equation is

$$Hu(y) = \epsilon u(y) ,$$

with

$$\epsilon = -\frac{Z^2}{(N+l+1)^2} ,$$

and

$$H = -\frac{d^2}{dy^2} + \frac{l(l+1)}{y^2} - \frac{2Z}{y} .$$

Solution

From lecture, we have

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{Ze^2}{r} \right) u(r) = Eu(r) .$$

We also know that

$$E_{nl} = E_{Nl} = -\frac{Z^2e^2}{2an^2} = -\frac{Z^2e^2}{2a(N+l+1)^2} ,$$

where N is the radial quantum number (which can be chosen independently of l) and n is the principal quantum number which must be greater than l; also, $a = \hbar^2/me^2$ is the Bohr radius. Multiply the radial Schroedinger equation above by $2a/e^2$ to get

$$\begin{aligned}
-\frac{Z^2}{(N+l+1)^2}u &= \left(-\frac{\hbar^2}{m}\frac{a}{e^2}\frac{d^2}{dr^2} + \frac{\hbar^2}{m}\frac{a}{e^2}\frac{l(l+1)}{r^2} - \frac{2Za}{r} \right) u \\
&= \left(-a^2\frac{d^2}{dr^2} + \frac{a^2}{r^2}l(l+1) - \frac{2Za}{r} \right) u = 0 \\
&= \left(-\frac{d^2}{dy^2} + \frac{l(l+1)}{y^2} - \frac{2Z}{y} \right) u .
\end{aligned}$$

End Solution

(b) To find $\left\langle 1/r^2 \right\rangle$ we just find $\left\langle 1/y^2 \right\rangle/a^2$ using the above $u(y)$, H, and ϵ and we evaluate $\left\langle 1/y^3 \right\rangle/a^3$ to find $\left\langle 1/r^3 \right\rangle$. Find $\left\langle 1/r^2 \right\rangle$. Hint: the trick is to differentiate the Schroedinger equation you obtained in part (a) with respect to l.

Solution

Taking the derivative, as suggested, we have,

$$\frac{\partial H}{\partial l} u + H \frac{\partial u}{\partial l} = \frac{\partial \epsilon}{\partial l} u + \epsilon \frac{\partial u}{\partial l} \,.$$

We take the dot product with u to obtain,

$$\left\langle u \,\middle|\, \frac{\partial H}{\partial l} u \right\rangle + \left\langle u \,\middle|\, H \frac{\partial u}{\partial l} \right\rangle = \left\langle u \,\middle|\, \frac{\partial \epsilon}{\partial l} u \right\rangle + \epsilon \left\langle u \,\middle|\, \frac{\partial u}{\partial l} \right\rangle \,.$$

We also have

$$\left\langle u \,\middle|\, H \frac{\partial u}{\partial l} \right\rangle = \left\langle H u \,\middle|\, \frac{\partial u}{\partial l} \right\rangle = \epsilon \left\langle u \,\middle|\, \frac{\partial u}{\partial l} \right\rangle \,,$$

Subtract from the previous equation to get

$$\left\langle u \,\middle|\, \frac{\partial H}{\partial l} u \right\rangle = \left\langle u \,\middle|\, \frac{\partial \epsilon}{\partial l} u \right\rangle \,.$$

Now,

$$\frac{\partial H}{\partial l} = \frac{2l+1}{y^2} \qquad \text{and} \qquad \frac{\partial \epsilon}{\partial l} = \frac{2Z^2}{(N+l+1)^3} = \frac{2Z^2}{n^3} \,,$$

from which we get

$$\left\langle \frac{2l+1}{y^2} \right\rangle = \frac{2Z^2}{n^3} \,,$$

or

$$\left\langle \frac{1}{r^2} \right\rangle_{nl} = \frac{2Z^2}{a^2 n^3 (2l+1)} \,.$$

Note that taking the partial derivative with respect to l was why we needed to write the energy as a function of N and l rather than n and l.

End Solution

(c) Find $\langle 1/r^3 \rangle$. Hint: this time the trick is to differentiate with respect to y.

Solution

Differentiating the Schroedinger equation with respect to y (and remembering that ϵ does not depend on y), we have

$$\frac{\partial H}{\partial y} u + H \frac{\partial u}{\partial y} = \epsilon \frac{\partial u}{\partial y} \,.$$

Take the dot product with u and use the fact that H is Hermitian,

$$\left\langle u \,\middle|\, \frac{\partial H}{\partial y} u \right\rangle + \left\langle u \,\middle|\, H \frac{\partial u}{\partial y} \right\rangle = \epsilon \left\langle u \,\middle|\, \frac{\partial u}{\partial y} \right\rangle \,,$$

or

$$\left\langle u \,\middle|\, \frac{\partial H}{\partial y} u \right\rangle + \left\langle Hu \,\middle|\, \frac{\partial u}{\partial y} \right\rangle = \epsilon \left\langle u \,\middle|\, \frac{\partial u}{\partial y} \right\rangle ,$$

or

$$\left\langle u \,\middle|\, \frac{\partial H}{\partial y} u \right\rangle + \epsilon \left\langle u \,\middle|\, \frac{\partial u}{\partial y} \right\rangle = \epsilon \left\langle u \,\middle|\, \frac{\partial u}{\partial y} \right\rangle ,$$

or

$$\left\langle u \,\middle|\, \frac{\partial H}{\partial y} u \right\rangle = 0 .$$

Now, as far as the above dot product is concerned,

$$\frac{\partial H}{\partial y} = -\frac{2l(l+1)}{y^3} + \frac{2Z}{y^2} .$$

(You might be wondering what happened to the third derivative term. That's what went with the $H\partial u/\partial y$ term!) We see

$$\left\langle \frac{1}{r^3} \right\rangle_{nl} = \frac{Z}{al(l+1)} \left\langle \frac{1}{r^2} \right\rangle_{nl} = \frac{2Z^3}{a^3 n^3 l(l+1)(2l+1)} .$$

End Solution

2. What the exchange term exchanges! Consider an excited state in helium in which the Coulomb shift plus exchange shift in the energy in the levels (relative to the hydrogen like levels with energy E) is

$$\Delta E = J - \frac{1}{2}(1 + \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2)K ,$$

where J is the Coulomb repulsion between the two electrons and K is the "exchange term." Suppose the initial spin state is $|\uparrow\rangle\,|\downarrow\rangle$. That is, electron 1 spin is up and electron 2 spin is down. What is the time evolution of the spin state? Hint: write the spin state as a superposition of the singlet and triplet spin states.

Solution

Let $|s\rangle$ and $|t\rangle$ stand for the singlet and triplet states. Then

$$|s\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle\,|\downarrow\rangle - |\downarrow\rangle\,|\uparrow\rangle) ,$$
$$|t\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle\,|\downarrow\rangle + |\downarrow\rangle\,|\uparrow\rangle) ,$$

Inverting,

$$|\tau = 0\rangle = |\uparrow\rangle\,|\downarrow\rangle = \frac{1}{\sqrt{2}}(|s\rangle + |t\rangle) ,$$

where we use τ for time so as not to confuse time with triplet! The singlet and triplet states are energy eigenstates, so we just insert the exponentials for the time dependence.

$$\omega_s = (E + J + K)/\hbar \quad \text{and} \quad \omega_t = (E + J - K)/\hbar\,.$$

The spin state at time t is then

$$\begin{aligned}
|\tau\rangle &= \frac{1}{\sqrt{2}}\Big(|s\rangle\, e^{-i\omega_s\tau} + |t\rangle\, e^{-i\omega_t\tau}\Big) \\
&= \frac{1}{2}\Big((|\uparrow\rangle\,|\downarrow\rangle - |\downarrow\rangle\,|\uparrow\rangle)\, e^{-i\omega_s\tau} + (|\uparrow\rangle\,|\downarrow\rangle + |\downarrow\rangle\,|\uparrow\rangle)\, e^{-i\omega_t\tau}\Big) \\
&= \frac{e^{-i(E+J)\tau/\hbar}}{2}\Big((|\uparrow\rangle\,|\downarrow\rangle - |\downarrow\rangle\,|\uparrow\rangle)\, e^{-iK\tau/\hbar} + (|\uparrow\rangle\,|\downarrow\rangle + |\downarrow\rangle\,|\uparrow\rangle)\, e^{+iK\tau/\hbar}\Big) \\
&= e^{-i(E+J)\tau/\hbar}\left(|\uparrow\rangle\,|\downarrow\rangle \cos(K\tau/\hbar) + i\,|\downarrow\rangle\,|\uparrow\rangle \sin(K\tau/\hbar)\right)\,.
\end{aligned}$$

We see that the spin state oscillates from pure up down to pure down up with a frequency $2K/\hbar$ (why is there a factor of two?) or a period $T = \pi\hbar/K$. The stronger the exchange term, the faster the "spins are exchanged between the electrons."

——— End Solution ———