PERTURBING THE WAVE FUNCTION (STARK EFFECT AND PROTON ELECTRIC DIPOLE MOMENT)

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 6.40.

When we derived the equations for first order perturbation theory, we got an expression for the correction ψ_{n1} to the wave function:

$$H_0\psi_{n1} + H'\psi_{n0} = E_{n0}\psi_{n1} + E_{n1}\psi_{n0} \tag{0.1}$$

In the earlier derivation, we expanded ψ_{n1} as a series in terms of the unperturbed wave functions. However, in some cases it's possible to solve this equation directly. Consider again the Stark effect in hydrogen. We know that the first order correction is $E_{1,1} = 0$, and (expressing things in terms of the Bohr radius $a = 4\pi\varepsilon_0\hbar^2/me^2$):

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{\hbar^2}{mar} \tag{0.2}$$

$$H' = eE_{ext}r\cos\theta \tag{0.3}$$

$$E_{1,0} = -\frac{\hbar^2}{2ma^2} \tag{0.4}$$

$$\psi_{1,0} = \frac{1}{\sqrt{\pi}a^{3/2}}e^{-r/a} \tag{0.5}$$

The equation to solve is then

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{1,1} - \frac{\hbar^2}{mar}\psi_{1,1} + \frac{\hbar^2}{2ma^2}\psi_{1,1} = -eE_{ext}r\cos\theta\frac{1}{\sqrt{\pi}a^{3/2}}e^{-r/a} \tag{0.6}$$

We try a solution of form

$$\psi_{1,1} = \left(A + Br + Cr^2\right)e^{-r/a}\cos\theta \tag{0.7}$$

After calculating $\nabla^2\psi_{1,1}$ in spherical coordinates and cancelling off a common factor of $e^{-r/a}\cos\theta$ from both sides and multiplying through by r^2, we get

$$aA + r^2 B + \left(2r^3 - 2ar^2\right) C = -\frac{eE_{ext} m}{\sqrt{\pi a}\hbar^2} r^3 \tag{0.8}$$

Equating powers of r on each side, we get

$$A = 0 \tag{0.9}$$

$$B = 2aC \tag{0.10}$$

$$C = -\frac{eE_{ext} m}{2\sqrt{\pi a}\hbar^2} \tag{0.11}$$

$$B = -\frac{eE_{ext} m\sqrt{a}}{\sqrt{\pi}\hbar^2} \tag{0.12}$$

so the correction to the wave function is

$$\psi_{1,1} = -\frac{eE_{ext} m}{2\sqrt{\pi a}\hbar^2} \left(2ar + r^2\right) e^{-r/a} \cos\theta \tag{0.13}$$

The second order correction to the energy can be found from this equation that we got in the process of deriving second order perturbations:

$$\left\langle \psi_{1,0} \middle| H' \middle| \psi_{1,1} \right\rangle = E_{1,1} \left\langle \psi_{1,0} \middle| \psi_{1,1} \right\rangle + E_{1,2} \tag{0.14}$$

Since $E_{1,1} = 0$ we have

$$E_{1,2} = \left\langle \psi_{1,0} \middle| H' \middle| \psi_{1,1} \right\rangle \tag{0.15}$$

Plugging in the functions, we get

$$E_{1,2} = -\frac{e^2 E_{ext}^2 m}{2\sqrt{\pi a}\hbar^2} \frac{1}{\sqrt{\pi} a^{3/2}} \int_0^\infty \int_0^\pi \int_0^{2\pi} \left(2ar + r^2\right) e^{-2r/a} \cos^2\theta r^3 \sin\theta d\phi d\theta dr \tag{0.16}$$

This integral can be looked up or done with software, and the answer is

$$E_{1,2} = -\frac{9a^4 e^2 E_{ext}^2 m}{4\hbar^2} \tag{0.17}$$

As another example of a case where the equation can be solved exactly, suppose the proton had an electric dipole moment **p**. The potential due to a dipole is

$$V(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0 r^2}\mathbf{p}\cdot\hat{\mathbf{r}} \tag{0.18}$$

If $\mathbf{p}$ points in the z direction, then

$$V(\mathbf{r}) = \frac{p\cos\theta}{4\pi\varepsilon_0 r^2} \tag{0.19}$$

and the perturbation on the electron's hamiltonian is

$$H' = -eV = -\frac{ep\cos\theta}{4\pi\varepsilon_0 r^2} \tag{0.20}$$

The equation to solve has the same LHS as 0.6, but with a RHS using the new H':

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{1,1} - \frac{\hbar^2}{mar}\psi_{1,1} + \frac{\hbar^2}{2ma^2}\psi_{1,1} = -\frac{ep\cos\theta}{4\pi\varepsilon_0 r^2}\frac{1}{\sqrt{\pi}a^{3/2}}e^{-r/a} \tag{0.21}$$

Trying the same form for a solution as in 0.7 we get by the same calculation as above:

$$aA + r^2 B + \left(2r^3 - 2ar^2\right)C = \frac{mep}{4\pi\varepsilon_0\hbar^2\sqrt{\pi a}} \tag{0.22}$$

This time, the RHS is a constant, so

$$A = \frac{mep}{4\pi\varepsilon_0\hbar^2\sqrt{\pi a^3}} \tag{0.23}$$

$$B = C = 0 \tag{0.24}$$

and the correction to the wave function is

$$\psi_{1,1} = \frac{mep}{4\pi\varepsilon_0\hbar^2\sqrt{\pi a^3}}e^{-r/a}\cos\theta \tag{0.25}$$

The average dipole moment of the hydrogen atom is (treating the proton and electron as point charges):

$$\mathbf{p}_H = -e\mathbf{r} \tag{0.26}$$

$$= -er\left(\sin\theta\cos\phi\hat{\mathbf{x}} + \sin\theta\sin\phi\hat{\mathbf{y}} + \cos\theta\hat{\mathbf{z}}\right) \tag{0.27}$$

The average $\langle \mathbf{p}_H \rangle$ can be calculated using the unperturbed wave function plus the first order correction:

$$\langle \mathbf{p}_H \rangle = \left\langle \psi_{1,0} + \psi_{1,1} \right| \mathbf{p}_H \left| \psi_{1,0} + \psi_{1,1} \right\rangle \tag{0.28}$$

The x and y components average out to zero due to the integrals over ϕ, so we're left with (using Maple for the integrals):

$$\langle \mathbf{p}_H \rangle = -e\hat{\mathbf{z}} \left\langle \psi_{1,0} + \psi_{1,1} \right| r\cos\theta \left| \psi_{1,0} + \psi_{1,1} \right\rangle \tag{0.29}$$

$$= -\frac{me^2ap}{4\pi\varepsilon_0\hbar^2}\hat{\mathbf{z}} \tag{0.30}$$

$$= -\mathbf{p} \tag{0.31}$$

where we've used $a = 4\pi\varepsilon_0\hbar^2/me^2$ to get the last line. Thus the total electric dipole moment of the atom is zero.

The first-order correction to the energy is $\left\langle \psi_{1,0} \right| H' \left| \psi_{1,0} \right\rangle = 0$ (due to the integral over θ being zero), so as above, we can use 0.15 to calculate the second-order energy correction as before:

$$E_{1,2} = \left\langle \psi_{1,0} \right| H' \left| \psi_{1,1} \right\rangle \tag{0.32}$$

$$= -\frac{me^2p^2}{24\left(\pi\varepsilon_0\hbar a\right)^2} \tag{0.33}$$

$$= -\frac{2p^2\hbar^2}{3me^2a^4} \tag{0.34}$$

$$= \frac{4}{3}\left(\frac{p}{ea}\right)^2 E_{1,0} \tag{0.35}$$