Example: The polarizibility of the ground state H-atom

- Suppose H-atom is in the ground state, and apply E-field along the z-axis. Calculate the 1st order correction to wave function and 2nd correction to energy, electric dipole, and polarizibility.



Solution: In the absence of E-field, the ground state is

$$\psi^0 = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}, \quad \text{where } a = \frac{\hbar^2}{me^2}, \quad \text{and } E_0 = -\frac{e^2}{2a}.$$

$$H_0 \psi^0 = \left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r}\right)\psi^0 = E^0 \psi^0.$$

- The external field can be viewed as a perturbation. (Please think why?)

$$H' = -e\mathcal{E} z = -e\mathcal{E} r \cos\theta.$$

Certainly, the 1st order correction of energy vanishes $\langle \psi^0 | e\mathcal{E} r\cos\theta | \psi^0 \rangle = 0$. (parity selection rule)

If we calculate the 2nd correction to Energy and 1st order correction to wavefunctions directly using the formulas, we need to sum all the matrix elements such as

$$\langle \psi_{np}^{0} | e\mathcal{E} z | \psi_{0s} \rangle \quad \text{for all the } n \geq 1.$$

- (Why we only care about the p-level? Check Wigner-Eckert).

We will use a better way to calculate the polarizibility

According to the relation $[H_0 - E^{(0)}]\psi^{(1)} = (E^{(1)} - H')\psi^{(0)}$

where $H = H_0 + H'$, and $\psi = \psi^{(0)} + \psi^{(1)} + \cdots$ (we absorb the small parameter $\lambda$ in $H'$ and $\psi^{(1)}$). In our case $E^{(1)} = 0 \Rightarrow$

$(H_0 - E^0)\psi^{(1)} = e\mathcal{E} r\cos\theta\,\psi^{(0)}$. We will directly solve this Eq.

Because $H_0$, $\psi^{(0)}$ are spherical symmetric, $\psi^{(1)}$ has to ~~d~~ in the angular form of $\propto \cos\theta$. We set $\boxed{\psi^{(1)} = \psi^{(0)} f(r)\cos\theta} \Rightarrow$

$$\nabla^2\psi^{(1)} = f(r)\cos\theta\,\nabla^2\psi^{(0)} + \psi^{(0)}\nabla^2(f(r)\cos\theta) + 2[\nabla\cos\theta f(r)]\nabla\psi^{(0)}$$

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{\hat{\ell}^2}{r^2\hbar^2}, \quad \cos\theta \propto Y_{10}$$

$$\nabla^2[f(r)\cos\theta] = \cos\theta\left[\frac{1}{r}\frac{d^2}{dr^2}(rf) - \frac{2}{r^2}f\right]$$ why 2 not 1?

$$[\vec{\nabla}\cos\theta\, f(r)]\cdot\vec{\nabla}\psi^{(0)} = \cos\theta\frac{df}{dr}\cdot\frac{d\psi^{(0)}}{dr} = -\frac{\cos\theta}{a}\frac{df}{dr}\psi^{(0)}$$

only has radial component

plug in $\psi^{(0)} \propto e^{-r/a}$

$$\Rightarrow \left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} - E^0\right]\psi^{(1)}$$

$$= \underbrace{-\frac{\hbar^2}{2m}f(r)\cos\theta\left[\nabla^2 - \frac{e^2}{r} - E^0\right]\psi^{(0)}}_{=0} - \frac{\hbar^2}{2m}\cos\theta\left[\frac{1}{r}\frac{d^2}{dr^2}(rf) - \frac{2}{r^2}f\right]\psi^{(0)}$$

$$-\frac{\hbar^2}{m}\left(\frac{-\cos\theta}{a}\right)\frac{df}{dr}\psi^{(0)} = e\mathcal{E} r\cos\theta\,\psi^{(0)}$$

$$\Rightarrow \quad \frac{1}{2r}\frac{d^2}{dr^2}(rf) - \frac{1}{a}\frac{df}{dr} - \frac{f}{r^2} = -\frac{\mathcal{E}}{ea} r \qquad \left[ \text{remember } a = \frac{\hbar^2}{me^2} \right]$$

$f$ needs to satisfy the boundary condition that $\lim_{r\to 0} f(r) = 0$, otherwise $\psi^{(1)}$ is not regular over angular variable as $r \to 0$.

Or we can know this the $\psi^{(1)}$ belong to $\psi_{np}$ for $n \geq 1$, thus all of them vanish at $r = 0$.

$f(r) = 0$ as $r \to 0$.

Try series solution $f(r) = \sum_{n=1}^{\infty} C_n r^n$

$$\frac{1}{2}\sum_{n=1}^{\infty} C_n (n+1) n \, r^{n-2} - \frac{1}{a}\sum_{n=1}^{\infty} C_n n \, r^{n-1} - \sum_{n=1}^{\infty} C_n r^{n-2} = -\frac{\mathcal{E}}{ea} r$$

$$\sum_{n=0}^{\infty} C_{n+1}\left[\frac{(n+1)(n+2)}{2} - 1\right] r^{n-1} - \frac{1}{a}\sum_{n=1}^{\infty} n C_n r^{n-1} = -\frac{\mathcal{E}}{ea} r$$

$$\Rightarrow \quad \sum_{n=1}^{\infty} \left\{ C_{n+1}\left[\frac{(n+1)(n+2)}{2} - 1\right] - \frac{1}{a} n C_n \right\} r^{n-1} = -\frac{\mathcal{E}}{ea} r$$

$2C_2 - \frac{C_1}{a} = 0$ — we can set $C_{n\geq 3} = 0$

$5C_3 - \frac{2C_2}{a} = -\frac{\mathcal{E}}{ea}$ — and $C_2 = \frac{\mathcal{E}}{2e}$

$9C_4 - 3\frac{C_3}{a} = 6$ — $C_1 = 2aC_2 = \frac{a}{e}\mathcal{E}$

$\vdots$

$$\Rightarrow f(r) = \frac{\mathcal{E}a}{e} r + \frac{\mathcal{E}}{2e} r^2 = \frac{\mathcal{E}a^2}{e}\left[\left(\frac{r}{a}\right) + \frac{1}{2}\left(\frac{r}{a}\right)^2\right]$$

$$\Rightarrow \quad \psi^{(1)} = \frac{\mathcal{E}a^2}{e}\left[\left(\frac{r}{a}\right) + \frac{1}{2}\left(\frac{r}{a}\right)^2\right] \psi^{(0)} \cos\theta$$

According to $\quad E^{(2)} = \langle \psi^{(0)}, H' \psi^{(1)} \rangle \leftarrow$ Please check!

$$\Rightarrow E^{(2)} = -e\mathcal{E} \langle \psi^{(0)} | \, r \cos^2\theta \, f(r) \, \psi^{(0)} \rangle$$

$$= -\frac{e\mathcal{E}}{3} \langle \psi^{(0)} | \, r f(r) \, \psi^{(0)} \rangle = -\frac{e\mathcal{E}^2}{3} a^3 \left( \psi^{(0)}, \left[\left(\frac{r}{a}\right)^2 + \frac{1}{2}\left(\frac{r}{a}\right)^3\right) \psi^{(0)} \right)$$

$$= -\frac{1}{3} \mathcal{E}^2 a^3 \left[3 + \frac{15}{4}\right] = -\frac{9}{4} \mathcal{E}^2 a^3$$

$$\vec{D} = +e\vec{r} \quad \Rightarrow \langle D \rangle = +e\frac{(\psi, r_z \psi)}{(\psi, \psi)} = -\frac{e(\psi^{(0)} + \psi^{(1)}, r_z \, \psi^{(0)} + \psi^{(1)})}{(\psi^{(0)} + \psi^{(1)}, \psi^{(0)} + \psi^{(1)})}$$

$$\sim +2e(\psi^{(0)}, r_z \psi^{(1)}) = +\frac{2}{\mathcal{E}} E^{(2)} = \frac{9}{2} \mathcal{E} a^3$$

$$\boxed{\underset{\text{polarlibility}}{\chi} = -\frac{\partial^2}{\partial \mathcal{E}^2} E = \frac{9}{2} a^3}$$