10.36: Variational Calculation for the Polarizability of the Hydrogen Atom

In this exercise the polarizability of the hydrogen atom is calculated according to the procedure outlined in Problem 8-31 in the second edition of McQuarrie′s Quantum Chemistry. In the interest of clarity of mathematical expression atomic units are used:

$$e = me = h/2\pi = 4\pi\varepsilon_o = 1.$$

Polarizability, α, is a measure of the distortion of the electron density in the presence of an electric field. The interaction (perturbation) energy due to a field of strength ε with the hydrogen atom electron is easily shown to be:

$$E = \frac{-\alpha\varepsilon^2}{2}$$

Given that the ground state energy of the hydrogen atom is -0.5, in the presence of the electric field we would expect the electronic energy of the perturbed hydrogen atom to be,

$$E_{H\ atom} = \frac{-1}{2} - \frac{\alpha\varepsilon^2}{2}$$

It is assumed that the field direction is along the z axis. In this case the operator for the interaction of the external field with the electron density is, in spherical coordinates,

$$H' = \varepsilon r \cos(\theta)$$

Thus the total energy operator for the hydrogen atom in the presence of an electric field is this term plus the kinetic and electron-nucleus operator.

$$H = \frac{-1}{2r}\frac{d^2}{dr^2}(r\blacksquare) - \frac{1}{2r^2\sin(\theta)}\frac{d}{d\theta}\left(\sin(\theta)\frac{d}{d\theta}\blacksquare\right) - \frac{1}{2r^2\sin(\theta)^2}\frac{d^2}{d\phi^2}\blacksquare - \frac{1}{r}\blacksquare + \varepsilon r \cos(\theta)\blacksquare$$

The empty place holders indicate the location of the wave function to be operated on.

In the absence of the electric field the hydrogen atom is in the 1s electronic state. The field distorts (polarizes) the electron density and this can be modeled by assuming that in the presence of the external field the electron is in a state which is a superposition of the 1s and 2p$_z$ electronic states.

$$\Phi(r) = c_1\psi_{1s}(r) + c_2\psi_{2pz}(r,\theta)$$

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi}}exp(-r) \quad \psi_{2pz}(r,\theta) = \frac{1}{\sqrt{32\pi}}(r)exp\left(-\frac{r}{2}\right)\cos(\theta)$$

Within the variational method, using such a trial wave function requires solving the following secular determinant.

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

Due to normalization, orthogonality and symmetry we know that: $H_{12} = H_{21}$; $S_{11} = S_{22} = 1$; $S_{12} = S_{21} = 0$. We now evaluate H_{11}, H_{12} and H_{22} and solve the secular determinant.

$$H_{11} = \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{1s}(r) \begin{bmatrix} -\frac{1}{2r}\frac{d^2}{dr^2}(r\psi_{1s}(r))\dots \\ +\frac{-1}{2r^2\sin(\theta)}\left[\frac{d}{d\theta}\sin(\theta)\frac{d}{d\theta}\psi_{1s}(r)\right] \\ +\frac{-1}{2r^2\sin(\theta)^2}\frac{d^2}{d\phi^2}\psi_{1s}(r) \end{bmatrix} r^2 sin(\theta)d\,phid\theta dr \dots \rightarrow \frac{-1}{2} + \int_0^\infty \int_0^\pi$$

$$\int_0^{2\pi} \psi_{1s}(r)\left(-\frac{1}{r} + \varepsilon r \cos(\theta)\right)\psi_{1s}(r)r^2\sin(\theta)d\phi d\theta dr$$

$$H_{12} = \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{1s}(r) \left[\begin{array}{c} -\frac{1}{2r}\frac{d^2}{dr^2}(r\psi_{2pz}(r,\theta))\dots \\ +\frac{-1}{2r^2\sin(\theta)}\left[\frac{d}{d\theta}\sin(\theta)\frac{d}{d\theta}\psi_{2pz}(r,\theta)\right] \\ +\frac{-1}{2r^2\sin(\theta)^2}\frac{d^2}{d\phi^2}\psi_{2pz}(r,\theta) \end{array} \right] r^2\sin(\theta)d\,phi d\theta dr\dots \to \frac{128}{243}2^{\frac{1}{2}}\varepsilon + \int_0^\infty \int_0^\pi$$

$$\int_0^{2\pi} \psi_{1s}(r)\left(-\frac{1}{r}+\varepsilon r\cos(\theta)\right)\psi_{2pz}(r,\theta)r^2\sin(\theta)d\phi d\theta dr$$

$$H_{22} = \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{2pz}(r,\theta) \left[\begin{array}{c} -\frac{1}{2r}\frac{d^2}{dr^2}(r\psi_{2pz}(r,\theta))\dots \\ +\frac{-1}{2r^2\sin(\theta)}\left[\frac{d}{d\theta}\sin(\theta)\frac{d}{d\theta}\psi_{2pz}(r,\theta)\right] \\ +\frac{-1}{2r^2\sin(\theta)^2}\frac{d^2}{d\phi^2}\psi_{2pz}(r,\theta) \end{array} \right] r^2\sin(\theta)d\,phi d\theta dr\dots \to \frac{-1}{8} + \int_0^\infty \int_0^\pi$$

$$\int_0^{2\pi} \psi_{2pz}(r,\theta)\left(-\frac{1}{r}+\varepsilon r\cos(\theta)\right)\psi_{2pz}(r,\theta)r^2\sin(\theta)d\phi d\theta dr$$

Solving the secular determinant for the energy eigenvalues:

$$\left|\begin{pmatrix} H_{11}-E & H_{12} \\ H_{12} & H_{22}-E \end{pmatrix}\right| = 0\Big|_{float,\,4}^{solve,\,E} \left[\begin{array}{c} (-.3125)+.2572e(-3)(.5314e6+.8389e7\varepsilon^2)^{\frac{1}{2}} \\ (-.3125)-.2572e(-3)(.5314e6+.8389e7\varepsilon^2)^{\frac{1}{2}} \end{array}\right]$$

The lowest energy eigenvalue is expanded in ε in order to compare the variational calculation with equation 2.

$$(-.3125 - .2572e - 3\left(.5314e6 + .8389e7\varepsilon^2\right)^{\frac{1}{2}}$$

This comparison shows that, in atomic units, α has the value of 2.96. This value is in error by 35% when compared to the experimental result of 4.0. Although it is not apparent when atomic units are used, this calculation does reveal that atomic polarizability is proportional to atomic volume.