87(6): Estimating the Charge Density, Second Method

This method is similar to note 87(4), the only difference is that the probability of finding an electron in a spherical shell is now estimated from:

$$\text{prob} = 4\pi r^2 R^2(r) \quad - (1)$$

and the normalized probability is defined (i.e. chosen) to be:

$$\text{prob(normalized)} := 4\pi \left(\frac{r}{a_0}\right)^2 R^2(r) - (2)$$

The effect of r(vac) is then:

$$\text{prob(normalized)} = 4\pi \left(\frac{r + r(\text{vac})}{a_0}\right)^2 R^2(r) - (3)$$

because it has been assumed in the basic method that R(r) is hydrogenic, so r inside R(r) does not change.

This method aims at defining electron densities in various orbitals. The electron density in each orbital is different and defined by:

$$N = 4\pi \left(\frac{r + r(\text{vac})}{a_0}\right)^2 R^2(r) \quad - (4)$$

Finally the charge density is evaluated using:

$$\rho = \frac{eN}{V} \quad \rightarrow (5)$$

where V is an appropriate volume. This volume is also different for each orbital. To evaluate this volume self-consistently, it could be defined by:

$$V = \frac{4}{3}\pi \left(r + r(vdc)\right)^3_{max} \quad \rightarrow (6)$$

for each orbital, where $\left(r + r(vdc)\right)_{max}$ is the point at which N is a maximum.

Having evaluated the charge density it is next used in the driving term (the right hand side) of the equation:

$$\frac{d^2\phi}{dr^2} + \frac{1}{r}\frac{d\phi}{dr} - \frac{1}{r^2}\phi = -\frac{\rho}{\epsilon_0} \quad \rightarrow (7)$$

It is known from paper 63 that this is an Euler Bernulli resonance equation. Resonance occurs irrespective of the magnitude of ρ, which initially

is known to be very small, because the relativistic correction in H produces a 4×10^{-7} change, or splitting, of 2s from 2p. However, at resonance, ϕ may become very large, however small ρ is initially. If ϕ is very large and positive, and if it is denoted ϕ_{res}, then the Schrödinger equation of the H atom becomes:

$$-\frac{\hbar^2}{2m}\left(1+\frac{\alpha}{2\pi}\right)\frac{d^2P}{dr^2} + \left(V_{eff}^{(0)} + e\phi_{res}\right)P = EP \quad \text{---(8)}$$

where:

$$V_{eff}^{(0)} = -\frac{e^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2mr^2} \quad \text{---(10)}$$

By hypothesis, (8) is equivalent to:

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2P}{dr^2} + \left(V_{eff} + e\phi_{res}\right)P = EP} \quad \text{---(11)}$$

where:

$$V_{eff} = \frac{-e^2}{4\pi\epsilon_0\left(r + r(vac)\right)} + \frac{l(l+1)\hbar^2}{2m\left(r + r(vac)\right)^2} \quad \text{---(12)}$$

Discussion

By solving eqn. (11) it can be shown that at resonance, the H atom ionizes. The circuit needed to produce this resonance is set up from eqn. (7) and the material is chosen so that it is a solid state material that ionizes easily. For such a material, density functional code is modelled on the equation given here for H. Some discussion of this density functional code was given in paper 63. In eqn. (8):

$$\alpha = \langle \alpha \rangle \left(1 + \cos\left(K_0 r\right)\right) \quad -(13)$$

where K_0 is a characteristic wavenumber of the relative coordinate. The latter makes the electron wobble in each orbital, and this wobbling is represented in eqn. (13) by a cosine.

In paper 63 an Euler transform:

$$Kr = \exp(iKR) \quad -(14)$$

was applied to eqn. (7), so it becomes

5)

$$\frac{d^2\phi}{dR^2} + \kappa^2\phi = \frac{\rho(0)}{\epsilon_0}\exp(2i\kappa R) \quad -(15)$$

As it stands, eq (15) will not resonate unless $\rho(0)$ is oscillatory, for example cosical. This oscillatory driving term is obtained from the radiative correction, i.e. from eqs. (4) and (5):

$$\rho(0) = \frac{4\pi e}{V}\left(\frac{r + r(vac)}{a_0}\right)^2 R^2(r). \quad -(16)$$

To make eq. (16) consistent with eq. (15), the Euler transform (14) must be used in eq. (16):

$$\kappa_1(r + r(vac)) = \exp\left(i\kappa_1(R + R(vac))\right). \quad -(17)$$

$$-(18)$$

where: $\kappa_1 \neq \kappa$.

Thus:

$$r + r(vac) = \frac{1}{\kappa_1}\cos\left(\kappa_1(R + R(vac))\right) \quad -(19)$$

and eq. (15) is:

6)

$$\frac{d^2\phi}{dR^2} + k^2\phi =$$

$$= \frac{4\pi\rho}{\epsilon_0 \bar{V}} \left(\frac{\cos^2\left(k_1\left(R + R(vac)\right)\right)}{a_0^2 k_1^2} \right) \exp\left(2ikR\right)$$

— (20)

The functional dependence of r on $r(vac)$ is found from:

$$-\frac{\hbar^2}{2m}\left(1 + \frac{\alpha}{2\pi}\right)\frac{d^2P}{dr^2} + \bar{V}_{eff}^{(0)} P = EP \quad — (21)$$

i.e. $$-\frac{\hbar^2}{2m}\frac{d^2P}{dr^2} + \bar{V}_{eff} P = EP \quad — (22)$$

i.e: $$-\frac{\hbar^2 \alpha}{4\pi m}\frac{d^2P}{dr^2} + \left(\bar{V}_{eff}^{(0)} - \bar{V}_{eff}\right) P = 0$$

— (23)

and the resonant ϕ from eqn. (20) used finally in eqn. (8).