V. THE HYDROGEN ATOM IN THE ELECTRIC FIELD – VARIATIONAL APPROACH

Polarization of an atom or molecule can be calculated by using the finite field method described on p. 639. Let us apply this method to the hydrogen atom. Its polarizability was already calculated using a simple version of perturbation theory (p. 636). This time we will use the variational method.

The Hamiltonian for the isolated hydrogen atom (within the Born–Oppenheimer approximation) reads as

$$\hat{H}^{(0)} = -\frac{1}{2}\Delta_e - \frac{1}{r},$$

where the first term is the electronic kinetic energy operator, and the second its Coulomb interaction energy with the nucleus (proton–electron distance is denoted by r). The atom is in a homogeneous electric field $\mathcal{E} = (0, 0, \mathcal{E})$ with $\mathcal{E} > 0$ and as in perturbation theory (p. 636), the total Hamiltonian has the form

$$\hat{H} = \hat{H}^{(0)} + V$$

with $V = z\mathcal{E}$, where z denotes the coordinate of the electron and the proton is at the origin (the derivation of the formula is given on p. 636, the exchange of z to x does not matter).

The variational wave function ψ is proposed in the form

$$\psi = \chi_1 + c\chi_2, \tag{V.1}$$

where $\chi_1 = \frac{1}{\sqrt{\pi}}\exp(-r)$ is the $1s$ orbital of the hydrogen atom (ground state) and χ_2 is the normalized[1] p-type orbital

$$\chi_2 = Nz\exp(-\zeta r).$$

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[1] N can be easily calculated from the normalization condition

$$1 = N^2 \int \left[z\exp(-\zeta r)\right]^2 dV = N^2 \int_0^\infty dr\, r^4 \exp(-2\zeta r) \int_0^\pi d\theta \sin\theta \cos^2\theta \int_0^{2\pi} d\phi$$

$$= N^2 4!\,(2\zeta)^{-5}\frac{2}{3}2\pi = N^2 \frac{\pi}{\zeta^5}.$$

This gives $N = \sqrt{\frac{\zeta^5}{\pi}}$.

There are two variational parameters c and ζ. Let us assume for a while that we have fixed the value of ζ, so the only variational parameter is c. The wave function ψ is a linear combination of two expansion functions ("two-state model"): χ_1 and χ_2. Therefore, optimal energy follows from the Ritz method, according to case III of Appendix D on p. 948:

$$E = E_{\text{ar}} \pm \sqrt{\Delta^2 + h^2}, \tag{V.2}$$

where arithmetic mean energy $E_{\text{ar}} \equiv \frac{H_{11}+H_{22}}{2}$, while $\Delta \equiv \frac{H_{11}-H_{22}}{2}$ and $h \equiv H_{12} = H_{21}$ with

$$H_{ij} \equiv \langle \chi_i | \hat{H} \chi_j \rangle = \langle \chi_i | \hat{H}^{(0)} \chi_j \rangle + \langle \chi_i | V \chi_j \rangle.$$

Let us calculate all the ingredients of the energy given by (V.2).

First, let us note that $H_{11} \equiv \langle \chi_1 | \hat{H}^{(0)} \chi_1 \rangle = -\frac{1}{2}$ a.u., since χ_1 is the ground state of the isolated hydrogen atom (p. 178), and $V_{11} = \langle \chi_1 | V \chi_1 \rangle = 0$, because the integrand is antisymmetric with respect to $z \to -z$.

Now let us calculate $H_{22} = H_{22}^{(0)} + V_{22}$. Note that $V_{22} = 0$, for the same reason as V_{11}. We have

$$H_{22}^{(0)} = -\frac{1}{2} \langle \chi_2 | \Delta_e \chi_2 \rangle - \left\langle \chi_2 \left| \frac{1}{r} \chi_2 \right. \right\rangle.$$

The second integral is

$$\left\langle \chi_2 \left| \frac{1}{r} \chi_2 \right. \right\rangle = N^2 \int_0^\infty \mathrm{d}r \, r^3 \exp(-2\zeta r) \int_0^\pi \mathrm{d}\theta \, \sin\theta \cos^2\theta \int_0^{2\pi} \mathrm{d}\phi$$

$$= \frac{\zeta^5}{\pi} \cdot 3!(2\zeta)^{-4} \cdot \frac{2}{3} \cdot 2\pi = \frac{1}{2}\zeta,$$

where the dots separate the values of the corresponding integrals.[2] In Appendix R, the reader will find the main ingredients needed to calculate the first integral of $H_{22}^{(0)}$:

$$\langle \chi_2 | \Delta_e \chi_2 \rangle = N^2 \left\langle r\cos\theta \exp(-\zeta r) \left| \left[\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \sin\theta \frac{\partial}{\partial \theta} \right. \right. \right.$$

$$\left. \left. + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] r\cos\theta \exp(-\zeta r) \right\rangle$$

$$= N^2 \left[\begin{array}{c} \langle r\cos\theta \exp(-\zeta r) | \cos\theta \frac{1}{r^2} \frac{\partial}{\partial r} [r^2 \exp(-\zeta r) - \zeta r^3 \exp(-\zeta r)\rangle + \\ \langle r\cos\theta \exp(-\zeta r) | \frac{(-2\cos\theta)}{r^2} r \exp(-\zeta r)\rangle + 0 \end{array} \right]$$

$$= N^2 \left[\left\langle r\cos\theta \exp(-\zeta r) \left| \cos\theta \left[\frac{2}{r} - \zeta - 3\zeta + \zeta^2 r \right] \exp(-\zeta r) \right. \right\rangle \right]$$

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[2]Note that, in spherical coordinates, the volume element $\mathrm{d}V = r^2 \sin\theta \, \mathrm{d}r \, \mathrm{d}\theta \, \mathrm{d}\phi$. In derivations of this Appendix (and not only) we often use the equality $\int_0^\infty \mathrm{d}x \, x^n \exp(-\alpha r) = n! \alpha^{-(n+1)}$.

$$+ \left\langle r \cos\theta \exp(-\zeta r) \left| \frac{(-2\cos\theta)}{r} \exp(-\zeta r) \right. \right\rangle \right]$$

$$= \frac{\zeta^5}{\pi} \left(\frac{2}{3} \cdot 2\pi \right) \left[\frac{2 \cdot 2}{(2\zeta)^3} - \frac{4\zeta \cdot 3!}{(2\zeta)^4} + \frac{\zeta^2 \cdot 4!}{(2\zeta)^5} - \frac{2 \cdot 2!}{(2\zeta)^3} \right]$$

$$= -\zeta^2.$$

Thus, we obtain $H_{22} = \frac{1}{2}\zeta^2 - \frac{1}{2}\zeta$. This formula looks good, since for $\chi_2 = 2p_z$, i.e. for $\zeta = \frac{1}{2}$ we get correctly (see p. 178) $H_{22} = E_{2p} = -\frac{1}{8}$ a.u., the energy of orbital $2p$.

Let us turn to the non-diagonal matrix element of the Hamiltonian: $H_{12} = H_{12}^{(0)} + V_{12}$. Note, that $H_{12}^{(0)} = 0$, because χ_1 is an eigenfunction of $\hat{H}^{(0)}$ and $\langle \chi_1 | \chi_2 \rangle = 0$. Thus,

$$h = N\mathcal{E} \left\langle r \cos\theta \exp(-\zeta) \left| r \cos\theta \frac{1}{\sqrt{\pi}} \exp(-r) \right. \right\rangle$$

$$= N\mathcal{E} \frac{1}{\sqrt{\pi}} \int_0^\infty dr\, r^4 \exp\left[-(\zeta+1)r\right] \int_0^\pi d\theta\, \sin\theta \cos^2\theta \int_0^{2\pi} d\phi$$

$$= \mathcal{E} \frac{\sqrt{\zeta^5}}{\pi} \cdot 4!(\zeta+1)^{-5} \cdot \frac{2}{3} \cdot 2\pi = 32 \frac{\sqrt{\zeta^5}}{(\zeta+1)^5} \mathcal{E}.$$

Now we can write eq. (V.2) as a function of ζ:

$$E = \frac{1}{4}(\zeta^2 - \zeta - 1) - \sqrt{\frac{1}{16}(\zeta^2 - \zeta + 1)^2 + \zeta^5 \left(\frac{2}{\zeta+1} \right)^{10} \mathcal{E}^2}. \qquad \text{(V.3)}$$

We would like to expand this expression in a power series of $\mathcal{E}$ to highlight the coefficient at $\mathcal{E}^2$, because this coefficient is related to the polarizability. The expansion gives (in a.u.)

$$E \approx \frac{1}{4}(\zeta^2 - \zeta - 1) - \frac{1}{4}(\zeta^2 - \zeta + 1) - \frac{1}{2}\alpha_{zz}\mathcal{E}^2 + \cdots = -\frac{1}{2} - \frac{1}{2}\alpha_{zz}\mathcal{E}^2 + \cdots,$$

where, according to eq. (12.24), the polarizability (in a.u.) reads as

$$\alpha_{zz} = 4 \cdot \frac{\zeta^5}{|\zeta^2 - \zeta + 1|} \left(\frac{2}{\zeta+1} \right)^{10}. \qquad \text{(V.4)}$$

Several numerical values of α_{zz} calculated using (V.3) and (V.4), are given on p. 639. They may be compared with the exact result $\alpha_{zz} = 4.5$ a.u.