

## *Hydrogen Atom in Electric Field—The Variational Approach*

Polarization of an atom or molecule can be calculated by using the finite field (FF) method described on p. 746. Let us apply this method to the hydrogen atom. Its polarizability was already calculated by using a simple version of the perturbation theory (p. 743). 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 is its Coulomb interaction energy with the nucleus (with proton-electron distance is denoted by  $r$ ). The atom is in the uniform electric field  $\mathcal{E} = (0, 0, \mathcal{E})$ , with  $\mathcal{E} > 0$ , and similarly, as it was in the perturbation theory (p. 744), 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 in the origin (the derivation of the formula is given on p. 743, and the exchange of  $z$  to  $x$  does not matter).

The variational wave function  $\psi$  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  $\chi_2$  is the normalized <sup>1</sup>  $p$ -type orbital

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

There are two variational parameters  $c$  and  $\zeta$ . Let us assume for a while that we have fixed the value of  $\zeta$  so that the only variational parameter is  $c$ . The wave function  $\psi$  is a linear combination of two expansion functions (“*two-state model*”):  $\chi_1$  and  $\chi_2$ . Therefore, the optimal

<sup>1</sup>  $N$  can be easily calculated from the normalization condition  $1 = N^2 \int [z \exp(-\zeta r)]^2 dV = N^2 \int_0^\infty dr r^4 \exp(-2\zeta r) \int_0^\pi d\theta \sin \theta \cos^2 \theta \int_0^{2\pi} d\phi = N^2 4! (2\zeta)^{-5} \frac{2}{3} 2\pi = N^2 \frac{\pi}{\zeta^5}$ . This gives  $N = \sqrt{\frac{\zeta^5}{\pi}}$ .

energy follows from the Ritz method according to case III of see [Appendix D](https://booksite.elsevier.com/978-0-444-59436-5) available at [booksite.elsevier.com/978-0-444-59436-5](https://booksite.elsevier.com/978-0-444-59436-5) on p. e63:

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

where arithmetic mean energy  $E_{ar} \equiv \frac{H_{11}+H_{22}}{2}$ , 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 compute all the ingredients of the energy given by Eq. (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  $\chi_1$  is the ground state of the isolated hydrogen atom (p. 203), and  $\langle \chi_1 | V | \chi_1 \rangle = 0$  because the integrand is antisymmetric with respect to  $z \rightarrow -z$ .

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

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

The second integral is  $\langle \chi_2 | \frac{1}{r} | \chi_2 \rangle = N^2 \int_0^\infty dr r^3 \exp(-2\zeta r) \int_0^\pi d\theta \sin \theta \cos^2 \theta \int_0^{2\pi} d\phi = \frac{\zeta^5}{\pi} \cdot 3! (2\zeta)^{-4} \cdot \frac{2}{3} \cdot 2\pi = \frac{1}{2} \zeta$ , where the dots separate the values of the corresponding integrals.<sup>2</sup> In [Appendix R](https://booksite.elsevier.com/978-0-444-59436-5) available at [booksite.elsevier.com/978-0-444-59436-5](https://booksite.elsevier.com/978-0-444-59436-5), the reader will find the main ingredients needed to compute the first integral of  $H_{22}^{(0)}$ :

$$\begin{aligned} \langle \chi_2 | \Delta_e | \chi_2 \rangle &= N^2 \left\langle r \cos \theta \exp(-\zeta r) \left| \left[ \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right. \right. \right. \\ &\quad \left. \left. \left. + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] r \cos \theta \exp(-\zeta r) \right\rangle \\ &= N^2 \left[ \left\langle r \cos \theta \exp(-\zeta r) \left| \cos \theta \frac{1}{r^2} \frac{\partial}{\partial r} [r^2 \exp(-\zeta r) - \zeta r^3 \exp(-\zeta r)] \right\rangle \right. \\ &\quad \left. + \left\langle r \cos \theta \exp(-\zeta r) \left| \frac{(-2 \cos \theta)}{r^2} r \exp(-\zeta r) \right\rangle + 0 \right. \right] \\ &= N^2 \left[ \left\langle r \cos \theta \exp(-\zeta r) \left| \cos \theta \left[ \frac{2}{r} - \zeta - 3\zeta + \zeta^2 r \right] \exp(-\zeta r) \right\rangle \right. \\ &\quad \left. + \left\langle r \cos \theta \exp(-\zeta r) \left| \frac{(-2 \cos \theta)}{r} \exp(-\zeta r) \right\rangle \right] \\ &= \frac{\zeta^5}{\pi} \left( \frac{2}{3} \cdot 2\pi \right) \left[ 2 \cdot 2 \cdot (2\zeta)^{-3} - 4\zeta \cdot 3! \cdot (2\zeta)^{-4} \right. \\ &\quad \left. + \zeta^2 \cdot 4! \cdot (2\zeta)^{-5} - 2 \cdot 2! \cdot (2\zeta)^{-3} \right] = -\zeta^2. \end{aligned}$$

<sup>2</sup> Note that in the spherical coordinates, the volume element  $dV = r^2 \sin \theta dr d\theta d\phi$ . We have used the equality  $\int_0^\infty dr r^n \exp(-ar) = n! a^{-(n+1)}$ .

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 (see p. 203)  $H_{22} = E_{2p} = -\frac{1}{8}$  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  $\chi_1$  is an eigenfunction of  $\hat{H}^{(0)}$  and  $\langle \chi_1 | \chi_2 \rangle = 0$ . Thus,  $h = N\mathcal{E} \langle r \cos \theta \exp(-\zeta r) | r \cos \theta \frac{1}{\sqrt{\pi}} \exp(-r) \rangle = N\mathcal{E} \frac{1}{\sqrt{\pi}} \int_0^\infty dr r^4 \exp[-(\zeta + 1)r] \int_0^\pi d\theta \sin \theta \cos^2 \theta \int_0^{2\pi} d\phi = \mathcal{E} \frac{\sqrt{\zeta^5}}{\pi} \cdot 4!(\zeta + 1)^{-5} \cdot \frac{2}{3} \cdot 2\pi = 32 \frac{\sqrt{\zeta^5}}{(\zeta + 1)^5} \mathcal{E}$ .

Now we can write Eq. (V.2) as a function of  $\zeta$ :

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

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

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

where according to Eq. (12.24) the polarizability (in atomic units) reads as

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

Several numerical values of  $\alpha_{zz}$  computed by using Eqs. (V.3) and (V.4) are given on p. 746. They are compared with the exact result  $\alpha_{zz} = 4.5$  a.u.

