HYDROGEN ATOM IN A CRYSTAL LATTICE

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 6.39.

We'll look here at a crude model of a hydrogen atom embedded within a crystal lattice. The model simulates a crystal by placing the hydrogen atom at the origin and then placing pairs of charges on the three coordinate axes. We put equal charges q_1 at $x = \pm d_1$, q_2 at $y = \pm d_2$ and q_3 at $z = \pm d_3$. Consider first the charges on the x axis. The potential caused by them at the location (x, y, z) of the electron in the hydrogen atom is

$$V_x = -\frac{eq_1}{4\pi\epsilon_0}\left(\frac{1}{\sqrt{(d_1 - x)^2 + y^2 + z^2}} + \frac{1}{\sqrt{(-d_1 - x)^2 + y^2 + z^2}}\right) \tag{1}$$

Assuming that all the distances $d_i \gg r = \sqrt{x^2 + y^2 + z^2}$ we can approximate this potential by

$$V_x = -\frac{eq_1}{4\pi\epsilon_0 d_1}\left(\frac{1}{\sqrt{\left(1 - \frac{x}{d_1}\right)^2 + \frac{y^2}{d_1^2} + \frac{z^2}{d_1^2}}} + \frac{1}{\sqrt{\left(-1 - \frac{x}{d_1}\right)^2 + \frac{y^2}{d_1^2} + \frac{z^2}{d_1^2}}}\right) \tag{2}$$

$$\approx -\frac{eq_1}{4\pi\epsilon_0 d_1}\left(2 + 2\frac{x^2}{d_1^2} - \frac{y^2}{d_1^2} - \frac{z^2}{d_1^2}\right) \tag{3}$$

$$= \beta_1\left(2d_1^2 + 2x^2 - y^2 - z^2\right) \tag{4}$$

$$= 2\beta_1 d_1^2 + 3\beta_1 x^2 - \beta_1 r^2 \tag{5}$$

where

$$\beta_i \equiv -\frac{eq_i}{4\pi\epsilon_0 d_i^3} \tag{6}$$

We can do a similar calculation for the y and z charges, with the result

$$H' = V_0 + 3\left(\beta_1 x^2 + \beta_2 y^2 + \beta_3 z^2\right) - \left(\beta_1 + \beta_2 + \beta_3\right) r^2 \tag{7}$$

$$V_0 \equiv 2\left(\beta_1 d_1^2 + \beta_2 d_2^2 + \beta_3 d_3^2\right) \tag{8}$$

As we now have the perturbation hamiltonian, we can use non-degenerate perturbation theory to work out the energy correction on the ground state. As we set up the hydrogen wave functions in Maple in an earlier post, we can use that to do the integrals. To do this, we first express the rectangular coordinates in terms of spherical coordinates and then calculate the integral using spherical coordinates. The result is

$$\langle 100| H' |100\rangle = V_0 \tag{9}$$

For the $n = 2$ states, we need to use degenerate perturbation theory, but again we can use our Maple code to calculate the matrix W. With the states listed in the order $|200\rangle, |211\rangle, |210\rangle, |21-1\rangle$ we get

$$W = \begin{bmatrix} V_0 & 0 & 0 & 0 \\ 0 & V_0 + 6a^2\left(\beta_1 + \beta_2 - 2\beta_3\right) & 0 & 18a^2\left(\beta_1 - \beta_2\right) \\ 0 & 0 & V_0 + 12a^2\left(-\beta_1 - \beta_2 + 2\beta_3\right) & 0 \\ 0 & 18a^2\left(\beta_1 - \beta_2\right) & 0 & V_0 + 6a^2\left(\beta_1 + \beta_2 - 2\beta_3\right) \end{bmatrix} \tag{10}$$

The eigenvalues are V_0, $V_0 + 12a^2\left(-\beta_1 - \beta_2 + 2\beta_3\right)$, $V_0 + 12a^2\left(-\beta_1 + 2\beta_2 - \beta_3\right)$ and $V_0 + 12a^2\left(2\beta_1 - \beta_2 - \beta_3\right)$.

For the different types of crystal symmetry, we have:

(1) Cubic symmetry, where $\beta_1 = \beta_2 = \beta_3$. In this case all four energy levels reduce to V_0, so there is no splitting. The eigenvectors are just the four original unperturbed states, since the off-diagonal elements of W are all zero.
(2) Tetragonal symmetry, where $\beta_1 = \beta_2 \neq \beta_3$. In this case, the energies become V_0 and $V_0 + 12a^2\left(-2\beta_1 + 2\beta_3\right)$ each with degeneracy 1, and $V_0 + 12a^2\left(\beta_1 - \beta_3\right)$ with degeneracy 2. The eigenvectors (the 'good' states) are still the four unperturbed states since the off-diagonal elements of W are again zero, with $|211\rangle$ and $|210\rangle$ belonging to the degenerate energy $V_0 + 12a^2\left(\beta_1 - \beta_3\right)$, $|200\rangle$ to V_0 and $|21-1\rangle$ to $V_0 + 12a^2\left(-2\beta_1 + 2\beta_3\right)$.
(3) Orthorhombic symmetry, where all the β_i are different. In this case there are four distinct energies with eigenvectors as follows:

Energy	Eigenvector
V_0	$\|200\rangle$
$V_0 + 12a^2(-\beta_1 - \beta_2 + 2\beta_3)$	$\|210\rangle$
$V_0 + 12a^2(-\beta_1 + 2\beta_2 - \beta_3)$	$\frac{1}{\sqrt{2}}(-\|211\rangle + \|21-1\rangle)$
$V_0 + 12a^2(2\beta_1 - \beta_2 - \beta_3)$	$\frac{1}{\sqrt{2}}(\|211\rangle + \|21-1\rangle)$