251(3): Example Calculation of Expectation Value

In this note the expectation value:

$$E_1 = -\frac{e\hbar}{2m}\int \phi^* \underline{\sigma}\cdot\underline{B}_1 \phi \, d\tau \quad -(1)$$

is calculated for the excited state of the H atom represented by:

$$\phi = N x \exp(-\alpha r) \quad -(2)$$

Here:

$$\underline{\sigma}\cdot\underline{B}_1 = \underline{\sigma}\cdot\underline{B} - \frac{\underline{\sigma}\cdot\underline{r}\ \underline{r}\cdot\underline{B}}{r^2} \quad -(3)$$

Align $\underline{B}$ along Z so:

$$\frac{1}{r^2}\underline{\sigma}\cdot\underline{r}\ \underline{r}\cdot\underline{B} = \left(\frac{Z}{r}\right)^2 \sigma_Z B_Z \quad -(4)$$

$$= \cos^2\theta\, \sigma_Z B_Z$$

in spherical polar coordinates.

So:

$$E_1 = -\frac{e\hbar}{2m}\sigma_Z B_Z\left(\int \phi^*\phi\, d\tau - \int \phi^* \cos^2\theta\, \phi\, d\tau\right) \quad -(5)$$

First note that in spherical polar coordinates:

$$x = r\sin\theta\cos\phi \quad -(6)$$

and

$$d\tau = r^2 dr \sin\theta\, d\theta\, d\phi \quad -(7)$$

) The space is spanned by:

$$0 \leq r \leq \infty, \quad 0 \leq \theta \leq \pi, \quad 0 \leq \phi \leq 2\pi \quad -(8)$$

Note the integrals:

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \quad -(9)$$

$$\int_0^\pi \cos^n\theta \sin\theta \, d\theta = \frac{\left(1+(-1)^n\right)}{n+1} \quad -(10)$$

$$\int_0^{2\pi} \cos^2\phi \, d\phi = \frac{\phi}{2} + \frac{1}{2}\sin 2\phi \Big|_0^{2\pi} = \pi \quad -(11)$$

Therefore:

$$\int \phi^* \phi \, d\tau = N^2 \int x^2 \exp(-2\alpha r) d\tau \quad -(12)$$

$$= N^2 \int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\phi \, r^4 \sin^3\theta \cos^2\phi \, e^{-2\alpha r}$$

$$= N^2 \int_0^\infty r^4 e^{-2\alpha r} dr \int_0^\pi (1-\cos^2\theta)\sin\theta \, d\theta \int_0^{2\pi} \cos^2\phi \, d\phi$$

$$= N^2 \frac{4!}{2^5 \alpha^5} \cdot \frac{4}{3} \pi = \frac{N^2 \pi}{\alpha^5}$$

The normalization condition is:

$$N = \left(\frac{\alpha^5}{\pi}\right)^{1/2} \quad -(13)$$

3) which means
$$\int \phi^* \phi \, d\tau = 1 \quad -(14)$$

Similarly, using:
$$\phi = \left(\frac{\alpha^5}{\pi}\right)^{1/2} x \exp(-\alpha r) \quad -(15)$$

it is found that:
$$\int \phi^* \cos^2\theta \, \phi \, d\tau = \frac{1}{3} \quad -(16)$$

Therefore:
$$\boxed{E_1 = -\frac{e\hbar}{3m} \sigma_Z B_Z} \quad -(17)$$

For the wavefunction (2) the resonance frequency is
$$\omega_1 = \frac{2}{3} \frac{e B_Z}{m} \quad -(18)$$

and has been shifted from the ESR frequency:
$$\omega = \frac{e B_Z}{m} \quad -(19)$$

Using computer algebra, this calculation can be repeated for the hydrogenic wavefunctions, ensuring that each is carefully normalized.

4) The hydrogenic wavefunctions are:

$$\phi(r,\theta,\phi) = R(r)\,Y(\theta,\phi) \quad -(20)$$

where R are the radial functions and Y the spherical harmonics. The first few radial functions are as follows.

Table 1

n	ℓ	$R_{n\ell}(r)$
1	0 (1s)	$\left(\frac{Z}{a}\right)^{3/2} 2\exp\left(-\frac{\rho}{2}\right)$
2	0 (2s)	$\left(\frac{Z}{a}\right)^{3/2} \frac{1}{2\sqrt{2}}(2-\rho)\exp\left(-\frac{\rho}{2}\right)$
2	1 (2p)	$\left(\frac{Z}{a}\right)^{3/2} \frac{1}{2\sqrt{6}}\rho\exp\left(-\frac{\rho}{2}\right)$
3	0 (3s)	$\left(\frac{Z}{a}\right)^{3/2} \frac{1}{9\sqrt{3}}(6-6\rho+\rho^2)\exp\left(-\frac{\rho}{2}\right)$
3	1 (3p)	$\left(\frac{Z}{a}\right)^{3/2} \frac{1}{9\sqrt{6}}(4-\rho)\rho\exp\left(-\frac{\rho}{2}\right)$
3	2 (3d)	$\left(\frac{Z}{a}\right)^{3/2} \frac{1}{9\sqrt{30}}\rho^2\exp\left(-\frac{\rho}{2}\right)$

where

$$\rho = \left(\frac{2Z}{na}\right) r \quad -(21)$$

and

$$a = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} \quad -(22)$$

For an infinitely heavy nucleus $a = a_0$

5) is the Bohr radius, and the reduced mass μ becomes the electron mass. The R functions are related to the associated Laguerre functions L by:

$$R_{nl}(r) = -\left(\frac{2Z}{na}\right)\left[\frac{(n-l-1)!}{2n((n+l)!)^3}\right]\rho^{l} L_{n+l}^{2l+1} \exp\left(-\frac{\rho}{2}\right) \quad -(23)$$

The spherical harmonics are defined in general by:

$$Y_{lm_l} = \left(\frac{1}{2\pi}\right)^{1/2} \exp(i m_l \phi)\, \Theta_{lm_l}(\theta) \quad -(24)$$

where

$$\Theta_{lm_l}(\theta) = \left[\frac{(2l+1)(l-|m_l|)!}{2(l+|m_l|)!}\right] P_l^{|m_l|}(\cos\theta) \quad -(25)$$

where $P_l^{|m_l|}(\cos\theta)$ are the associated Legendre functions. The first few spherical harmonics are as follows:

Table 2

l	m_l	$Y_{lm_l}(\theta, \phi)$
0	0	$\frac{1}{2\pi^{1/2}}$
1	0	$\frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2} \cos\theta$

6)

Table 2 Continued

l	m_l	$Y_{lm_l}(\theta, \phi)$
1	± 1	$\mp \frac{1}{2}\left(\frac{3}{2\pi}\right)^{1/2} \sin\theta \exp(\pm i\phi)$
2	0	$\frac{1}{4}\left(\frac{5}{\pi}\right)^{1/2}\left(3\cos^2\theta - 1\right)$
2	± 1	$\mp \frac{1}{2}\left(\frac{15}{2\pi}\right)^{1/2} \cos\theta \sin\theta \exp(\pm i\phi)$
2	± 2	$\frac{1}{4}\left(\frac{15}{2\pi}\right)^{1/2} \sin^2\theta \exp(\pm 2i\phi)$
3	0	$\frac{1}{4}\left(\frac{7}{\pi}\right)^{1/2}\left(2 - 5\sin^2\theta\right) \cos\theta$
3	± 1	$\mp \frac{1}{8}\left(\frac{21}{\pi}\right)^{1/2}\left(5\cos^2\theta - 1\right) \sin\theta \exp(\pm i\phi)$
3	± 2	$\frac{1}{4}\left(\frac{105}{2\pi}\right)^{1/2} \cos\theta \sin^2\theta \exp(\pm 2i\phi)$
3	± 3	$\mp \frac{1}{3}\left(\frac{35}{\pi}\right)^{1/2} \sin^3\theta \exp(\pm 3i\phi)$

Example of a Complete Wavefunction : 2p

There are three 2p wavefunctions :

$$n = 2, \; l = 1, \; m_l = 0, \pm 1$$

so the three complete wavefunctions are found from Tables 1 and 2. For example :

$$\phi(n=2, l=1, m_l=0)$$

$$= \left(\frac{Z}{a}\right)^{3/2} \frac{1}{2\sqrt{6}} \rho \exp\left(-\rho/2\right) \cdot \frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2} \cos\theta$$

— (26)

$$= \frac{1}{4\sqrt{2\pi}} \left(\frac{Z_1}{a} \right)^{3/2} \rho \exp\left(-\frac{\rho}{2} \right) \cos\theta \quad - (27)$$

The computer algebra can now be used to evaluate eq. (5) for eq. (27). The first step is to check that eq. (27) gives the correct normalization:

$$\int \phi^* \phi \, d\tau = \underline{1} \quad - (28)$$

Then E_1 can be computed for all the hydrogenic wave functions using software to evaluate the associated Laguerre and Legendre polynomials. There should be different E_1 and resonance frequencies ω_1 for each orbital unless there is degeneracy.

<u>This</u> gives <u>rise to</u> a new <u>resonance technique</u>.