ESO(9): Energy Eigenvalues of the ESOR Hamiltonian

The ESOR Hamiltonian is:

$$\hat{H}\phi = \frac{e}{2\hbar m}\,\underline{\sigma}\cdot\left(\underline{B} - \frac{\underline{r}}{r^2}(\underline{r}\cdot\underline{B})\right)\hat{\underline{S}}\cdot\hat{\underline{L}}\,\phi \quad -(1)$$

and its expectation value is:

$$\langle\hat{H}\rangle = \frac{e}{2\hbar m}\int\phi^*\hat{H}\phi\, d\tau \quad -(2)$$

where the integration is carried out over all space. We use the result:

$$\hat{\underline{S}}\cdot\hat{\underline{L}}\,\phi = \frac{1}{2}\left(\hat{j}^2 - \hat{\ell}^2 - \hat{s}^2\right)\phi \quad -(3)$$

$$= \frac{\hbar^2}{2}\left(j(j+1) - \ell(\ell+1) - s(s+1)\right)\phi.$$

Therefore the energy eigenvalues from eq. (1) are:

$$E = \frac{e\hbar}{4m}\left(j(j+1)-\ell(\ell+1)-s(s+1)\right)\left[\underline{\sigma}\cdot\underline{B}\int\phi^*\phi\, d\tau - \int\phi^*\frac{\underline{\sigma}\cdot\underline{r}}{r^2}\,\underline{r}\cdot\underline{B}\,\phi\, d\tau\right] \quad -(4)$$

in which

$$\int\phi^*\phi\, d\tau = 1 \quad -(5)$$

In spherical polar coordinates:

a)

$$X = r\sin\theta\cos\phi$$
$$Y = r\sin\theta\sin\phi \quad -(6)$$
$$Z = r\cos\theta$$

and
$$\int f \, d\tau = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{0}^{\infty} f \, r^2 \sin\theta \, dr \, d\theta \, d\phi \quad -(7)$$

where
$$r^2 = X^2 + Y^2 + Z^2 \quad -(8)$$

If the magnetic field is aligned in the Z axis:
$$\frac{\underline{\sigma} \cdot \underline{r}}{r^2} \, \underline{r} \cdot \underline{B} = \frac{\sigma_Z Z^2 B_Z}{X^2 + Y^2 + Z^2} \quad -(9)$$

It can be assumed that on average:
$$\left\langle \frac{Z^2}{X^2 + Y^2 + Z^2} \right\rangle = \frac{1}{3} \quad -(10)$$

in which case eq. (4) reduces to:
$$E = \frac{e\hbar}{4m} \sigma_Z B_Z \left(j(j+1) - \ell(\ell+1) - s(s+1) \right) \left(1 - \frac{1}{3} \right) \quad -(11)$$
$$= \frac{1}{6} \frac{e\hbar}{m} \sigma_Z B_Z \left(j(j+1) - \ell(\ell+1) - s(s+1) \right)$$

which is eq. (15) of note 250(8).

More generally,
$$\frac{Z^2}{X^2 + Y^2 + Z^2} = \cos^2\theta \quad -(12)$$

3) in spherical polar coordinates, so:

$$\int \psi^* \frac{\underline{\sigma}\cdot\underline{r}}{r^2}\, \underline{r}\cdot\underline{B}\, \psi \, d\tau \qquad -(13)$$

$$= B_Z \sigma_Z \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\int_0^{a_0} \psi^* \cos^2\theta\, \psi\, r^2 \sin\theta \, dr\, d\theta\, d\phi$$

where the integral has been cut off at a_0 to give a finite result. Therefore this part of the ESR hamiltonian depends on which orbital is being considered. For example the $2p_Z$ orbital in atomic hydrogen is:

$$\psi_{2p_Z} = R_{21} Y_{10} = \frac{1}{4}\left(\frac{1}{2\pi a_0^3}\right)^{1/2} \frac{r}{a_0} \cos\theta \exp\left(-\frac{r}{2a_0}\right)$$

$$= \psi^*_{2p_Z} \qquad -(14)$$

so:

$$\int \psi^* \frac{\underline{\sigma}\cdot\underline{r}}{r^2}\, \underline{r}\cdot\underline{B}\, \psi\, d\tau = \frac{\sigma_Z B_Z}{16 a_0^5} \int_0^{a_0} r^4 \exp\left(-\frac{r}{a_0}\right) dr \int_0^{\pi} \cos^3\theta \sin\theta \, d\theta$$

The exact value of the integral depends on the upper bound of the dr integral. In the case

$$a_0 \to \infty \qquad -(14b)$$

the integral is

$$\int_0^{\infty} r^4 \exp\left(-\frac{r}{a_0}\right) dr \qquad -(14c)$$

4) Using the result:

$$\int \sin\theta \cos^3\theta \, d\theta \, d\theta = -\frac{1}{4}\cos^4\theta \quad -(16)$$

it is seen that for $2p_2$ in H:

$$\int \psi^* \frac{\underline{\sigma}\cdot\underline{r} \quad \underline{r}\cdot\underline{B}}{r^2}\psi \, d\tau = 0 \quad -(17)$$

This process can now be repeated for the H wavefunctions using computer algebra. The H wave functions are:

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \quad -(18)$$

where R are the radial functions and Y the spherical harmonics. These are very well known and only the first two are given here:

l	m_l	Y_{lm_l}
0	0	$\frac{1}{2\pi^{1/2}}$
1	0	$\frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2}\cos\theta$
	± 1	$\mp\frac{1}{2}\left(\frac{3}{2\pi}\right)^{1/2}\sin\theta \exp(\pm i\phi)$

For $l = 1$, $n = 2$:

$$R_{21} = \left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{1}{2\sqrt{6}}\right)\rho \exp\left(-\frac{\rho}{2}\right),$$

$$\rho = \frac{r}{a}$$