1)

178(3): Time Independent Perturbation Theory

In order to find the correct wavefunctions of H in a magnetic field, perturbation theory is needed. The unperturbed system is the H atom, described by:

$$\hat{H}^{(0)} \psi_n = E_n \psi_n , \qquad -(1)$$

$$n = 0, 1, 2, \ldots$$

The treatment given here is that given in Atkins, 2nd. ed., pp. 173 ff. The perturbed hamiltonian is:

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} + \ldots \qquad -(2)$$

More generally:

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)} + \ldots \qquad (3)$$

and

$$\psi = \psi_0 + \lambda \psi_0^{(1)} + \ldots \qquad (4)$$

$$E = E_0 + \lambda E_0^{(1)} + \ldots \qquad (5)$$

The Schroedinger equation is:

$$\hat{H} \psi = E \psi \qquad -(6)$$

i.e.

$$\left(\hat{H}^{(0)} + \lambda \hat{H}^{(1)} + \ldots\right)\left(\psi_0 + \lambda \psi_0^{(1)} + \ldots\right) = \left(E_0 + \lambda E_0^{(1)} + \ldots\right)\left(\psi_0 + \lambda \psi_0^{(1)} + \ldots\right) \qquad -(7)$$

or:

$$\hat{H}^{(0)} \psi_0 = E_0 \psi_0 \qquad -(8)$$

$$\left(\hat{H}^{(0)} - E_0\right) \psi_0^{(1)} = \left(E_0^{(1)} - \hat{H}^{(1)}\right) \psi_0 \qquad -(9)$$

$$\vdots$$

The first order correction $\psi_0^{(1)}$ is assumed to be:

2)

$$\phi_0^{(1)} = \sum_n a_n \phi_n \quad -(10)$$

and the sum is over all the wave functions of the model system, e.g. H. From eq. (10) in eq. (9):

$$\sum_n a_n \left(\hat{H}^{(0)} - E_0\right)\phi_n = \sum_n a_n (E_n - E_0)\phi_n \quad -(11)$$
$$= \left(E_0^{(1)} - \hat{H}^{(1)}\right)\phi_0$$

Therefore

$$\sum_n a_n (E_n - E_0)\delta_{0n} = E_0^{(1)} - \int \phi_0^* \hat{H}^{(1)} \phi_0 \, d\tau \quad -(12)$$

the left hand side is zero by orthonormality so:

$$E_0^{(1)} = \int \phi_0^* \hat{H}^{(1)} \phi_0 \, d\tau \quad -(13)$$

For ease of notation:

$$\boxed{E_0^{(1)} = H_{00}^{(1)} = \int \phi_0^* \hat{H}^{(1)} \phi_0 \, d\tau} \quad -(14)$$

This is the first order energy level correction.

Similarly from eq. (11):

$$\int \phi_k^* \sum_n a_n (E_n - E_0)\phi_n \, d\tau = \int \phi_k^* \left(E_0^{(1)} - \hat{H}^{(1)}\right)\phi_0 \, d\tau \quad -(15)$$

For:

$$k = n \neq 0 \quad -(16)$$

$$\sum_n a_n (E_n - E_0) = \int \phi_n^* E_0^{(1)} \phi_0 \, d\tau - \int \phi_n^* \hat{H}^{(1)} \phi_0 \, d\tau$$
$$= -\int \phi_n^* \hat{H}^{(1)} \phi_0 \, d\tau \quad -(17)$$

Denote:

$$H_{k0}^{(1)} = \int \phi_k^* \hat{H}^{(1)} \phi_0 \, d\tau \quad -(18)$$

Therefore:

$$a_k = \frac{H_{k0}^{(1)}}{E_0 - E_k} \quad -(19)$$

and the first order correction to the wave function is:

$$\boxed{\phi = \phi_0 + \sum_k{}' \left(\frac{H_{k0}^{(1)}}{E_0 - E_k} \right) \phi_k}$$

$$-(20)$$

here $\sum_k{}'$ means a sum over all states excluding $k = 0$.

In eq. (20), $\phi_1, \ldots, \phi_k$ are known wavefunctions of the unperturbed H. Also in H, there is no $n = 0$ energy state. The energy states of H are:

$$E_n = -\frac{me^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2} \quad -(21)$$

In the presence of a perturbation:

$$\hat{H}_+^{(1)} = -\frac{e\hbar}{2m} B_z \quad -(22)$$

$$\hat{H}_-^{(1)} = \frac{e\hbar}{2m} B_z \quad -(23)$$

the Schroedinger equation becomes:

$$\left(\hat{H}^{(0)} + \hat{H}^{(1)}\right)\left(\phi_0 + \phi_0^{(1)}\right) = \left(E_0 + E_0^{(1)}\right)\left(\phi_0 + \phi_0^{(1)}\right).$$

$$-(24)$$

4) Now apply perturbation theory to the equation:

$$\hat{H}\phi = E\phi \quad -(25)$$

where

$$\hat{H} = \frac{\hat{p}^2}{2m} + V \mp \frac{e\hbar}{2m}\underline{\sigma}\cdot\underline{B}. \quad -(26)$$

The basic equation is:

$$\hat{H}^{(0)}\phi_0 = E_0\phi_0 \quad -(27)$$

where

$$\hat{H}^{(0)} = \frac{\hat{p}^2}{2m} + V(x) \quad -(28)$$

$$E_0 = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2n^2}. \quad -(29)$$

Write eq. (26) as:

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} \quad -(30)$$

where:

$$\hat{H}^{(1)} = \mp\frac{e\hbar}{2m}B_Z \quad -(31)$$

Write:

$$E = E_0 + E_0^{(1)} \quad -(32)$$

$$\phi = \phi_0 + \phi_0^{(1)} \quad -(33)$$

Then:

$$E_0^{(1)} = \int \phi_0^* \hat{H}^{(1)}\phi_0 \, d\tau = H^{(1)} \quad -(34)$$

i.e.

$$E_0^{(1)} = H^{(1)} \quad -(35)$$

Using eq. (9):

$$\hat{H}^{(0)}\phi_0^{(1)} = E_0\phi_0^{(1)} \quad -(36)$$

Comparing eqs. (27) and (36):

$$\phi_0 = \phi_0^{(1)} \quad -(37)$$

5) Therefore $\phi^{(1)}_0$ is the same as the wave function of the H atom. Therefore in eq. (10):

$$\phi\,(\text{H atom}) = \sum_n a_n \phi_n\,(\text{H atom}) \quad -(38)$$

so

$$n = 0 \quad -(39)$$

and

$$a_0 = 1. \quad -(40)$$

In this simple case eq. (25) can be written as two equations:

$$\left(\frac{p^2}{2m} + V\right)\phi = E\phi \quad -(41)$$

and

$$-\frac{e\hbar}{2m}\,\underline{\sigma}\cdot\underline{B}\,\phi = E^{(1)}\phi \quad -(42)$$

so eq. (25) can be written as:

$$\left(-\frac{\hbar^2}{2m} + V\right)\phi = \left(E + E^{(1)}\right)\phi. \quad -(43)$$

The force equation is therefore as in note 178(2):

$$\boxed{\left(\hat{H} - E - E^{(1)}\right)\frac{d\phi}{dx} = F\phi} \quad -(44)$$

and this checks the self consistency of note 178(2).