Multi-electron Atoms

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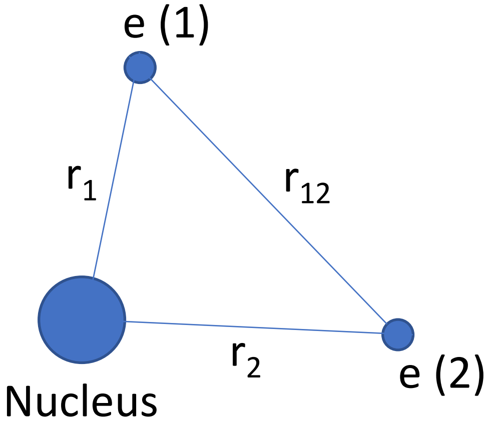
❑ Perturbation treatment of He atom



$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \qquad (1)$$

$$\hat{H} = \left(-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1}\right) + \left(-\frac{1}{2}\nabla_2^2 - \frac{Z}{2}\right) + \frac{1}{r_{12}}$$

$$\hat{H} = \underbrace{\hat{H}_1^0 + \hat{H}_2^0}_{\hat{H}^0} + \frac{1}{\underbrace{r_{12}}_{\hat{H}'}}$$

❑ Perturbation treatment of He atom

✓ Unperturbed Wave Function: Independent Electron Approximation

- Independent Electron Approximation

$$\hat{H}\psi(1,2,..,n) = E\psi(1,2,..,n)$$

$$\hat{H} = \sum_i \hat{H}_i\,, \qquad \psi = \prod_i \psi_i\,, \qquad E = \sum_i E_i\,, \qquad \widehat{H_i}\psi_i = E_i\psi_i$$

- Proof

$$\begin{aligned}\hat{H}\psi(1,2,..,n) &= \left(\hat{H}_1 + \hat{H}_2 + \cdots\right)\psi_1\psi_2\cdots \\ &= \hat{H}_1\psi_1\psi_2\cdots + \hat{H}_2\psi_1\psi_2\cdots + \cdots \\ &= \hat{H}_1\psi_1\psi_2\cdots + \psi_1\hat{H}_2\psi_2\cdots + \cdots \\ &= E_1\psi_1\psi_2\cdots + \psi_1E_2\psi_2\cdots + \cdots \\ &= E_1\psi_1\psi_2\cdots + E_2\psi_1\psi_2\cdots + \cdots \\ &= (E_1 + E_2 + \cdots)\psi_1\psi_1\psi_2\cdots \\ &= E\psi(1,2,..,n)\end{aligned}$$

❑ Perturbation treatment of He atom

$$\hat{H}^0 = \left(-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1}\right) + \left(-\frac{1}{2}\nabla_2^2 - \frac{Z}{2}\right)$$

$$\hat{H}' = \frac{1}{r_{12}}$$

$$\psi^0 = 1s(1)1s(2) = \frac{Z^3}{\pi}e^{-Zr_1}e^{-Zr_2} = \frac{Z^3}{\pi}e^{-Z(r_1+r_2)}$$

Now, what is the value of E^0?

$$E^0 = E_{1s}(1) + E_{1s}(2)$$

$$E^0 = 2 \times \left(-\frac{1}{2}Z^2\right) = -Z^2\ au$$

$$E^0 = -4\ au = -1.74 \times 10^{-17}J = -108.3\ eV$$

- The energy thus calculated is much below the experimentally observed value of $-1.25 \times 10^{-17}J = -78.4\ eV$
- Thus, first order correction is to be applied.

❑ Perturbation treatment of He atom

$$E^{(1)} = \int \psi^0 \hat{H}' \psi^0 d\tau = \int\int 1s(1)1s(2)\frac{1}{r_{12}}1s(1)1s(2)d\tau_1 d\tau_2$$

$$= \left(\frac{Z^3}{\pi}\right)^2 \int\int e^{-Z(r_1+r_2)}\frac{1}{r_{12}}e^{-Z(r_1+r_2)}d\tau_1 d\tau_2 = \frac{5}{8}Z$$

- ✓ The energy of He atom in ground state is, therefore

$$E_{1s^2} = -Z^2 + \frac{5}{8}Z = -2.75\ au = -74.8\ eV = -1.196 \times 10^{-17} J$$

- ✓ The error is 5%.
- ✓ The ionization of He is given by

$$He(1s^2) = He^+(1s) + e(1s)$$

$$IP = E_{1s}^{He^+} - E_{1s^2}^{He}$$

$$IP = -\frac{1}{2}Z^2 - \left(-Z^2 + \frac{5}{8}Z\right) = 0.75\ au = 20.4\ eV = 0.326\ J$$

- ✓ The experimental value is 24.6 eV or 0.393 J. Error is about 17%.
- ✓ A small error in total energy leads to a sufficiently large error in IP.

❑ Variation treatment of He atom

– The presence of one electron effectively reduces the nuclear charge of other electrons. For He atom, nuclear charge Z', instead of 2, can be considered as adjustable parameter.

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z'}{r_1} - \frac{Z'}{r_2} + \frac{1}{r_{12}}$$

$$= \left(-\frac{1}{2}\nabla_1^2 - \frac{Z'}{r_1}\right) + \left(-\frac{1}{2}\nabla_2^2 - \frac{Z'}{r_2}\right) + \frac{1}{r_{12}}$$

$$= \hat{H}(1) + \hat{H}(2) + \frac{1}{r_{12}}$$

✓ The trial function can be chosen by independent electron approximation

$$\psi = 1s(1)1s(2) = \frac{Z'^3}{\pi} e^{-Z'r_1} e^{-Z'r_2} = \frac{Z'^3}{\pi} e^{-Z'(r_1+r_2)}$$

✓ Using this trial function

$$E_{1s^2} = \frac{\int \psi \hat{H} \psi d\tau}{\int \psi^2 d\tau} = \int \psi \hat{H} \psi d\tau \quad [\psi \text{ is real and normalized}]$$

❑ Variation treatment of He atom

$$E_{1s^2} = \iint 1s(1)1s(2)\left[\hat{H}(1) + \hat{H}(2) + \frac{1}{r_{12}}\right]1s(1)1s(2)d\tau_1 d\tau_2$$

$$= \iint 1s(1)1s(2)\hat{H}(1)1s(1)1s(2)d\tau_1 d\tau_2$$

$$+ \iint 1s(1)1s(2)\hat{H}(2)1s(1)1s(2)d\tau_1 d\tau_2$$

$$+ \iint 1s(1)1s(2)\frac{1}{r_{12}}1s(1)1s(2)d\tau_1 d\tau_2$$

$$\Longrightarrow E_{1s^2} = \int 1s(1)\,\hat{H}(1)1s(1)d\tau_1 \underbrace{\int 1s(2)\,1s(2)d\tau_2}_{1}$$

$$+ \underbrace{\int 1s(1)\,1s(1)d\tau_1}_{1} \int 1s(2)\,\hat{H}(2)1s(2)d\tau_2 + J$$

Where, $\mathrm{J} = \iint 1s(1)1s(2)\frac{1}{r_{12}}1s(1)1s(2)d\tau_1 d\tau_2$

❑ Variation treatment of He atom

Since $\hat{H}(1)$ and $\hat{H}(2)$ are Hamiltonian of He^+ and they operate separately on electron 1 and 2.

$$\hat{H}(1)\psi(1) = E_{1s}^{He^+}(1)\psi(1)$$

$$\hat{H}(2)\psi(2) = E_{1s}^{He^+}(2)\psi(2)$$

Since $E_{1s}^{He^+}(1) = E_{1s}^{He^+}(2) = E_{1s}$

$$\Longrightarrow E_{1s^2} = E_{1s}\underbrace{\int 1s(1)\,1s(1)d\tau_1}_{1} + E_{1s}\underbrace{\int 1s(2)\,1s(2)d\tau_2}_{1} + J \Longrightarrow E_{1s^2}$$

$$= 2E_{1s} + J$$

E_{1s} of He^+in $1s$ state is given by

$$E_{1s} = \int 1s\left[-\frac{1}{2}\nabla^2 - \frac{Z}{r}\right]1sd\tau$$

$$= \int 1s\left[-\frac{1}{2}\nabla^2 - \frac{Z'}{r} + \left(\frac{Z'-Z}{r}\right)\right]1sd\tau$$

$$= \int 1s\left[-\frac{1}{2}\nabla^2 - \frac{Z'}{r}\right]1sd\tau + \int 1s\left(\frac{Z'-Z}{r}\right)1sd\tau$$

❑ Variation treatment of He atom

$$\Longrightarrow E_{1s} = -\frac{1}{2}Z'^2 + (Z' - Z)\int 1s\left(\frac{1}{r}\right)1s d\tau$$

Now,

$$\int 1s\left(\frac{1}{r}\right)1s d\tau = \frac{Z'^3}{\pi}\iiint e^{-Z'r}\left(\frac{1}{r}\right)e^{-Z'r}r^2\,\mathrm{drsin}\,\theta d\theta d\phi$$

$$= \frac{Z'^3}{\pi}\int_0^\infty e^{-2Z'r} r dr \underbrace{\int_0^\pi \sin\theta d\theta}_{2} \underbrace{\int_0^{2\pi} d\phi}_{2\pi}$$

$$= \frac{Z'^3}{\pi}4\pi\int_0^\infty e^{-2Z'r} r dr = 4Z'^3\frac{1}{(2Z')^2} = Z'$$

Therefore,

$$E_{1s^2} = 2 \times \left[-\frac{1}{2}Z'^2 + (Z' - Z)Z'\right] + \frac{5}{8}Z'$$

$$= -Z'^2 + 2Z'^2 - 2ZZ' + \frac{5}{8}Z'$$

$$= Z'^2 - 2ZZ' + \frac{5}{8}Z'$$

❑ Variation treatment of He atom

- By the principle of minimization

$$\frac{\partial E_{1s^2}}{\partial Z'} = 2Z' - 2Z + \frac{5}{8} = 0$$

$$\Longrightarrow Z' = Z - \frac{5}{16} = 2 - \frac{5}{16} = \frac{27}{16}$$

- The energy of He atom is

$$E_{1s^2} = \left(\frac{27}{16}\right)^2 - 2 \times 2 \times \frac{27}{16} + \frac{5}{8} \times \frac{27}{16}$$

$$= -2.84\, au$$

$$= -77.48\, eV$$

$$= -1.24 \times 10^{-17} J$$

- The error in total energy is reduced to 2%.
- IP is calculated to 23.06 eV or 0.369×10^{-17} J and the error is 6%.
- The screening effect

$$Z - Z' = 2 - \frac{27}{16} = \frac{5}{16} = 0.3125$$

❑ Antisymmetric wave function

He atom

- In ground state: $\Psi(1,2) = 1s(1)1s(2)$
- In excited state: $\Psi(1,2) = 1s(1)2s(2)$ (1)

  or, $\Psi(2,1) = 1s(2)2s(1)$ (2)
- Does the functions $\Psi(1,2)$ and $\Psi(2,1)$ have the same eigenvalues?
- Does the functions $\Psi(1,2)$ and $\Psi(2,1)$ have the same physical significance?
- $\Psi(1,2)$ and $\Psi(2,1)$ differ from each other. Their squares are also different. They lead to different probability distributions for the same two electrons in the same state.
- Does this make any physical sense? - **No.** Because electrons are indistinguishable.

❑ Antisymmetric wave function

- To make their physical senses, probability must not change on merely interchanging the electron positions, i.e.,

$$[\Psi(1,2)]^2 = [\Psi(2,1)]^2 \qquad (3)$$

This gives $\Psi(1,2) = \pm\Psi(2,1)$ (4)

- This means that functions (1) and (2) would be either the same or one be simply the negative of the other.
- If the function remains unchanged on interchange of electron positions it is ‘symmetric’.
- If it changes sign it is ‘antisymmetric’.
- Are these requirements met by the expressions (1) and (2)? No
- Their linear combinations (sum and difference) can met these requirements.

❑ Antisymmetric wave function

- $\Psi_+(\text{symmetric}) \quad = \frac{1}{\sqrt{2}}[1s(1)2s(2) + 1s(2)2s(1)]$ (5)
- $\Psi_-(\text{antisymmetric}) = \frac{1}{\sqrt{2}}[1s(1)2s(2) - 1s(2)2s(1)]$ (6)
- $\frac{1}{\sqrt{2}}$ is the normalization factor which can easily be derived as below:

$$\int \Psi^2 d\tau = \int \int [N\{1s(1)2s(2) \pm 1s(2)2s(1)\}]^2 d\tau_1 d\tau_2 = 1$$

Or, $N^2[\int 1s(1)^2 d\tau_1 \int 2s(2)^2 d\tau_2 + \int 1s(2)^2 d\tau_2 \int 2s(1)^2 d\tau_1$
$\pm 2\int 1s(1)2s(2) d\tau_1 \int 1s(2)2s(1) d\tau_2] = 1$

Or, $N^2[1 + 1 + 0] = 1$ or, $N = \frac{1}{\sqrt{2}}$.

- Which of the two wave functions (5) and (6) is to be used to describe the excited state of He when both lead to the same energy?

❑ Electron spin

- According to Goudsmith and Ulenbeck (1926), electron spins around its axis and its “spin angular momentum” or simply “spin” is given by

$$S = \sqrt{s(s+1)}\,\frac{h}{2\pi} \qquad (7)$$

- Spin angular momentum vector has three components, $S_x, S_y \text{ and } S_z$.
- By the quantum mechanics, only one of them can have specified value; and usually S_z is chosen.
- The possible values of S_z are $2s+1$, or 2; these values are given by $m_s\frac{h}{2\pi}$ (in SI unit), or m_s (atomic unit), where $m_s = \pm\frac{1}{2}$.
- The two states of electron corresponding to two quantum numbers $\pm\frac{1}{2}$ are degenerate; the degeneracy is broken in a magnetic field if the direction of field is taken as the *z*-axis.

❑ The Eigenvalue and Eigenfunctions of spin operator

- The quantity of interest, S_z is represented in quantum mechanics by its operator $\hat{S}_z$ and the Eigenvalues $m_s \frac{h}{2\pi}$.
- The eigenvalue equations are

$$\left.\begin{aligned} \hat{S}_z\alpha(s) &= \frac{1}{2}\frac{h}{2\pi}\alpha(s) \\ \hat{S}_z\beta(s) &= -\frac{1}{2}\frac{h}{2\pi}\beta(s) \end{aligned}\right\} \qquad (8)$$

where $\alpha(s)$ and $\beta(s)$ are the two eigenfunctions corresponding to the two eigenvalues.

- s within bracket refers to hypothetical spin coordinate and quite independent of the space coordinates.
- $\alpha(s)$ and $\beta(s)$ are usually written as α and β respectively, and are taken to be orthonormal, i.e.,

$$\int \alpha^2 ds = \int \beta^2 ds = 1 \text{ and } \int \alpha\beta ds = \int \beta\alpha ds = 0$$

❑ Spin-Orbitals

- An orbital does not give complete description of an electron. Because it can not describe the actual state.
- The complete wave function must represent the actual state of electron. It must give not only the probability of finding electron in space but also the probability of spin state, $\alpha(s)$ or $\beta(s)$.
- The actual state of an electron is represented by the product of the orbital and the spin functions. The product is called “spin-orbital”. Corresponding to an orbital ϕ, there will be two spin-orbitals $\phi\alpha$ and $\phi\beta$.
- For multi-electron atom, the spin state is represented by a product of individual spin functions. The operator for the *Z*-component is given by the sum of the operator for *Z*-components of individual electron, i.e.,

$$\hat{S}_z = \hat{S}_{1z} + \hat{S}_{2z} + \cdots\cdots$$

❑ Spin-Orbitals

- For two electron system, say He there are four possible spin functions viz.

$$\alpha(1)\alpha(2) \qquad (9)$$

$$\beta(1)\beta(2) \qquad (10)$$

$$\alpha(1)\beta(2) \qquad (11)$$

and $\alpha(2)\beta(2)$ (12)

- The eigenvalue for $\alpha(1)\alpha(2)$, for example, is

$$\hat{S}_z[\alpha(1)\alpha(2)] = (\hat{S}_{1z}+\hat{S}_{2z})[\alpha(1)\alpha(2)]$$

$$= \hat{S}_{1z}[\alpha(1)\alpha(2)] + \hat{S}_{2z}[\alpha(1)\alpha(2)]$$

$$= \alpha(2)\frac{1}{2}\alpha(1) + \alpha(1)\frac{1}{2}\alpha(2) = \alpha(1)\alpha(2)$$

- The eigenvalue (= 1) represents the *z*-component of the “total spin quantum number M_s $(= \sum m_s)$” and of the “angular momentum S_z $(= M_s \frac{h}{2\pi})$”.

Spin-Orbitals

Spin product functions	$M_s\ (=\sum m_s)$	$S_z(= M_s \frac{h}{2\pi})$
$\alpha(1)\alpha(2)$	$\frac{1}{2}+\frac{1}{2}$	$+1\frac{h}{2\pi}$
$\beta(1)\beta(2)$	$-\frac{1}{2}-\frac{1}{2}$	$-1\frac{h}{2\pi}$
$\alpha(1)\beta(2)$	$\frac{1}{2}-\frac{1}{2}$	0
$\alpha(2)\beta(1)$	$\frac{1}{2}-\frac{1}{2}$	0

- By arguments similar to orbital wave function, spin functions must be either symmetric or antisymmetric.
- Spin product functions in (9) and (10) are symmetric, but (11) and (12) are neither symmetric nor antisymmetric.
- In analogy with equations (5) and (6), the symmetric and antisymmetric spin functions can be obtained from the linear combination of product spin functions.

❑ Spin-Orbitals

- The four spin functions for two electron system are

Spin functions	M_s	
$\alpha(1)\alpha(2)$	+1	(13)
$\beta(1)\beta(2)$	-1	(14)
$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)+\alpha(2)\beta(1)]$	0	(15)
$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\alpha(2)\beta(1)]$	0	(16)

- The spin functions (13), (14) and (15) are symmetric, while the equation (16) is antisymmetric.

❑ Pauli principle and antisymmetric wave functions

- For the ground state of He, there are four possible product combinations of orbital and spin wave functions

$$1s(1)1s(2)[\alpha(1)\alpha(2)] \qquad (17)$$

$$1s(1)1s(2)[\beta(1)\beta(2)] \qquad (18)$$

$$1s(1)1s(2)\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)+\alpha(2)\beta(1)] \qquad (19)$$

$$1s(1)1s(2)\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\alpha(2)\beta(1)] \qquad (20)$$

- Which of these four combination will correctly represent the ground state of He?

- Let think about the following:

$$Symmetric(+)\times symmetric(+) = ?$$

$$Antisymmetric(-)\times antisymmetric(+) = ?$$

$$Antisymmetric(-)\times symmetric(+) = ?$$

❑ Pauli principle and antisymmetric wave functions

- According to W. Pauli “for a system more than two electrons the complete wave function including spin must be antisymmetric with respect to interchange of any two electron positions. ”
- It is, therefore, seen that the function (20) stands for the ground state of He.
- **For ground state** He, there are eight possible combination, of these following four are antisymmetric:

$$\Psi_1 = \frac{1}{2}[1s(1)2s(2) + 1s(2)2s(1)][\alpha(1)\beta(2) - \alpha(2)\beta(2)] \quad (21)$$

$$\Psi_2 = \frac{1}{\sqrt{2}}[1s(1)2s(2) - 1s(2)2s(1)][\alpha(1)\alpha(2)] \quad (22)$$

$$\Psi_3 = \frac{1}{\sqrt{2}}[1s(1)2s(2) - 1s(2)2s(1)][\beta(1)\beta(2)] \quad (23)$$

$$\Psi_1 = \frac{1}{2}[1s(1)2s(2) - 1s(2)2s(1)][\alpha(1)\beta(2) + \alpha(2)\beta(2)] \quad (24)$$

❑ Singlet and triplet state of He

- Energy of helium atom in excited state can be calculated as

$$\bar{E}_{1s2s} = \int \frac{\Psi^* \hat{H} \Psi d\tau}{\Psi^* \Psi} \qquad (25)$$

- En

❑Perturbation treatment

- Perturbation treatment of helium atom gives zeroth-order wave function by neglecting these repulsion and wave function would be the product of n hydrogenlike (one electron) orbital.

$$\psi^{(0)} = f_1(r_1, \theta_1, \phi_1) f_2(r_2, \theta_2, \phi_2) \cdots f_n(r_n, \theta_n, \phi_n) \qquad (2)$$

Where the hydrogenlike orbital are

$$\mathrm{f} = \mathrm{R_{nl}}(r) Y_l^m(\theta, \phi) \qquad (3)$$

- The approximate wave functions are qualitatively useful but it suffers from quantitative accuracy.
- This method uses full nuclear charge, which neglects the screening of electrons from nucleus.

❑Variational treatment

- The variational treatment of helium and lithium atoms gives considerable improved wave function because this treatment make use the effective nuclear charge for accounting the screening of electrons but it is still far from accurate wave function.

- In this technique, variation function that has the same form as eq. (2) but is not restricted to hydrogenlike or any other particular form of orbitals.

$$\phi = g_1(r_1, \theta_1, \phi_1) g_2(r_2, \theta_2, \phi_2) \cdots g_n(r_n, \theta_n, \phi_n) \qquad (4)$$

- Then it looks for the functions g_1, g_2, ……. g_n that minimize the variational integral

$$\int \phi^* \hat{H} \phi dv / \int \phi^* \phi dv \qquad (5)$$

❑Hartree self-consistent field (SCF) method

- This technique is basically same as variational treatment but more harder.
- The basic difference is that the trial functions for **Hartree SCF method include some parameters and these are varied.** On the other hand, variational treatment varies the functions g_i in eq. (4).

Let us consider the best possible atomic orbitals that are the product of a radial factor and a spherical harmonic

$$g_i = h_i(r_i) Y_{l_i}^{m_i}(\theta_i, \phi_i) \qquad (6)$$

- The procedure for calculating the g_i's was introduced by Hartree in 1928 and is called Hartree self-consistent-field (SCF) method. The proof that Hartree's procedure gives the best possible variation function of the form eq. (5) was given by Slater and Fock in 1930.

❑Hartree’s procedure

- The wave function of an atom containing n electrons is written as the product of n number of one-electron functions

$$\phi_0 = s_1(r_1, \theta_1, \phi_1) s_2(r_2, \theta_2, \phi_2) \cdots s_n(r_n, \theta_n, \phi_n) \qquad (1)$$

and the energy is

$$\mathrm{E} = \int \phi_0^* \hat{\mathrm{H}} \phi \mathrm{d}\tau \qquad (2)$$

If ϕ_0 is normalized which is ensured if each s_i is normalized function of r multiplied by a spherical harmonic, i.e.,

$$\int \mathrm{s}_\mathrm{i}^* \mathrm{s}_\mathrm{i} = 1 \qquad (3)$$

The best wavefunction is that which leads to minimum energy, i.e., which satisfies the equation

$$\delta \mathrm{E} = \delta \int \phi_0^* \hat{H} \phi d\tau = 0 \qquad (4)$$

for a small variation in any of the orbital.

Ĥ is the complete Hamiltonian given by

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - \sum_{i=1}^{n}\frac{Ze'^2}{r_i} + \frac{1}{2}\sum_{i=1}^{n}\sum_{i\neq j}^{n}\frac{e'^2}{r_{ij}} \qquad (5)$$

where an infinitely heavy point nucleus was assumed.

- ***The first sum in equation (5)*** contains the kinetic-energy operator for the n electrons.
- ***The second sum*** is the potential energy for the attractions between the electrons and the nucleus of charge Ze′; for a neutral atom, Z = n and $e'^2 = e^2/4\pi\varepsilon_0$.
- ***The last sum*** is the potential energy of the interelectronic repulsion; the restriction i ≠ j ignore the nonexistent self-repulsion (e'^2/r_{ii} or e'^2/r_{jj}) and the factor ½ average the same interelectronic repulsions like e'^2/r_{ij} and e'^2/r_{ji} .

- The Hamiltonian, Ĥ in equation (5) can be written as

$$\widehat{H} = \sum_{i}^{n} \widehat{H}_i^0 + \frac{1}{2}\sum_{i=1}^{n} \widehat{V}_i \qquad (6)$$

where,

$$\widehat{H}_i^0 = -\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{Ze'^2}{r_i} \qquad (7)$$

and

$$\widehat{V}_i = \sum_{i\neq j}^{n} \frac{e'^2}{r_{ij}} \qquad (8)$$

$\widehat{\mathrm{H}}_{\mathrm{i}}^0$ is hydrogen like Hamiltonian of the electron i and $\widehat{\mathrm{V}}_{\mathrm{i}}$ represents the total potential energy of the electron i due to repulsion by all other elctrons.

- To determine V_i in equation (8) Hartree assumes that each electron in the atom moves in a potential field due to the nucleus and all other electrons and assumed set of orbitals are

  $s_1, s_2, \ldots. s_n$

  which may be hydrogen like orbital.
- Now consider the electron 1 moving through the smeared cloud of other electrons.
- The potential energy of interaction between point charges Q_1 and Q_2

$$\mathrm{V}_{12} = \frac{Q_1 \; Q_2}{4\pi\epsilon_0 r_{12}} \qquad (9)$$

- For electron 1, $Q_1 = - e$, the electronic charge; and for electron 2, the infinitesimal charge in the infinitesimal volume $d\tau_2$ is $- e|s_2|^2 d\tau_2$. Summing up the interaction between Q_1 and infinitesimal elements of charge, we have

$$\mathrm{V}_{12} = \frac{\int(-e)(-e)|s_2|^2 d\tau_2}{4\pi\epsilon_0\, r_{12}} = e'^2 \frac{\int |s_2|^2 d\tau_2}{r_{12}} \tag{10}$$

where, $\mathrm{e}'^2 = \dfrac{e^2}{4\pi\epsilon_0}$

- Adding in the interactions with the other electron, we have

$$V_1 = \mathrm{V}_{12} + V_{13} + \cdots\cdots\cdots + V_{1n} = \sum_{j=2}^{n} e'^2 \frac{\left|s_j\right|^2}{r_{1j}} d\tau_j \tag{11}$$

- Under the central force field assumption *V_1* is a function of *r_1* only. Adding *V_1* with *$-Ze'^2/r_1$* and using as potential energy in a one-electron Schrodinger equation

$$\left[-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze'^2}{r_1} + V_1(r_1)\right] t_1(1) = \epsilon_1 t_1(1) \tag{12}$$

and solution for $t_1(1)$ will give improved orbital for electron 1.

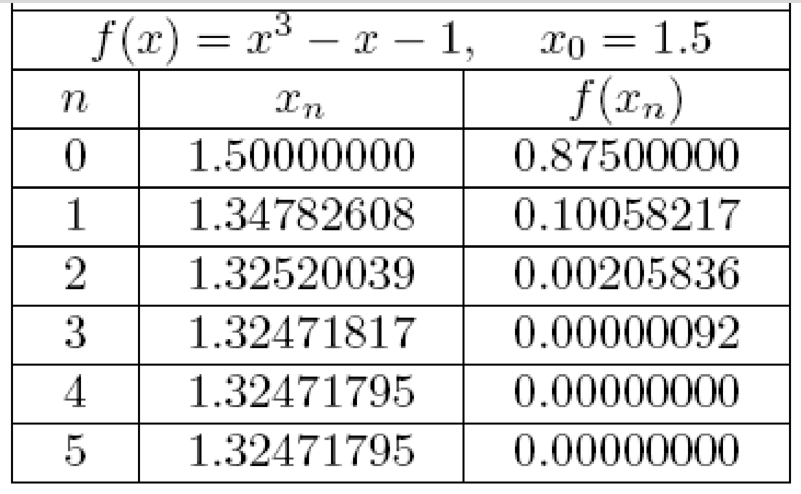
- However, the solution of equation (12) is very difficult because V_1 required the prior knowledge of all one electron wave functions. Hartree suggested an iteration method for solution.

Iteration method

Let us consider a function $x^3 = x + 1$

The iteration formula for this function can be written as

$$x_{n+1} = x_n - \frac{x_n^3 - x - 1}{3x_n^2 - 1}$$



$f(x) = x^3 - x - 1, \quad x_0 = 1.5$		
n	x_n	$f(x_n)$
0	1.50000000	0.87500000
1	1.34782608	0.10058217
2	1.32520039	0.00205836
3	1.32471817	0.00000092
4	1.32471795	0.00000000
5	1.32471795	0.00000000

- First V_1 is calculated from chosen set of functions s_1, s_2 ….s_n.
- Using V_1 in equation (12), $t_1(1)$ is calculated by a numerical method.
- We now go to electron 2 and regard it as moving in charge cloud of density

$$-e[|t_1(1)|^2 + |s_3|^2 + |s_4|^2 + \cdots + |s_n|^2]$$

due to the other electrons. Calculating $V_2(r_2)$ and solving a one-electron Schrodinger equation for electron 2 will give an improved orbital $t_2(2)$.

- This procedure is carried on until a set of improved orbitals for all n electrons is obtained.
- Then going back to electron 1 and repeating the process.
- This process of iteration is to be continued until the assumed set of s_i and the calculated set become identical. The final set of orbitals gives Hartree self-consistent-field wave functions (ϕ_i).
- Finally, we have the wave function

$$\Psi = \phi_1 \, \phi_2 \, \phi_3 \cdots\cdots \phi_n \qquad (13)$$

❑ Orbital energy and Total energy

The orbital energy ε_i of the electron *i* is

$$\varepsilon_i = \int \phi_i \widehat{H}_i \phi_i \, d\tau_i$$

$$= \int \phi_i \widehat{H}_i^0 \phi_i \, d\tau_i + \int \phi_i \left[\sum_{i \neq j} e'^2 \frac{\int \left|\phi_j\right|^2}{r_{ij}} \, d\tau_j \right] \phi_i \, d\tau_i$$

$$= \varepsilon_i^0 + \sum_{i \neq j} \int \int \frac{e'^2 |\phi_i|^2 \left|\phi_j\right|^2}{r_{ij}} \, d\tau_i \, d\tau_j$$

$$= \varepsilon_i^0 + \sum_{i \neq j} J_{ij} \qquad (14)$$

In equation (14), ε_i^0 is the orbital energy of the electron *i* in the absence of all other electrons, and J_{ij} is the average columbic energy of repulsion between two charges represented by $|\phi_i|^2$ and $\left|\phi_j\right|^2$.

The total energy of all the electron in the atom is

$$E = \int \Psi^* \, \hat{H} \, \Psi \, d\tau$$

$$= \int (\phi_1^* \, \phi_2^* \cdots \phi_n^*) \sum_i \hat{H}_i^0 \, (\phi_1 \, \phi_2 \cdots \phi_n) d\tau_1 \, d\tau_2 \cdots d\tau_n$$

$$+ \int (\phi_1^* \, \phi_2^* \cdots \phi_n^*) \frac{1}{2} \sum_i \sum_{i \neq j} \frac{e'^2}{r_{ij}} (\phi_1 \, \phi_2 \cdots \phi_n) d\tau_1 \, d\tau_2 \cdots d\tau_n$$

$$= \sum_i \varepsilon_i^0 + \frac{1}{2} \sum_i \sum_{i \neq j} \int \int e'^2 \frac{|\phi_i|^2 \left|\phi_j\right|^2}{r_{ij}} d\tau_i d\tau_j$$

$$= \sum_i \varepsilon_i^0 + \frac{1}{2} \sum_i \sum_{i \neq j} J_{ij} \qquad (15)$$

Operator $\hat{H}_i^0$ acts on electron *i* only and $\frac{1}{r_{ij}}$ on electrons *i* and *j,* and all orbitals are normalized.

❑ Relation between Orbital energy and Total energy

From equation (14), we get

$$\varepsilon_i^0 = \varepsilon_i - \sum_{i \neq j} J_{ij}$$

Inserting the value of ε_i^0 in equation (15) gives

$$E = \sum_i (\varepsilon_i - \sum_{i \neq j} J_{ij}) + \frac{1}{2} \sum_i \sum_{i \neq j} J_{ij}$$

$$= \sum_i \varepsilon_i - \sum_i \sum_{i \neq j} J_{ij} + \frac{1}{2} \sum_i \sum_{i \neq j} J_{ij}$$

$$= \sum_i \varepsilon_i - \frac{1}{2} \sum_i \sum_{i \neq j} J_{ij}$$

- ε_i involves, in addition to its own orbital energy in the field of the nucleus, the interaction with all other electrons in atoms. $\sum_i \varepsilon_i$ counts twice the interactions between electrons, like J_{ij} and J_{ji}. To obtain the correct energy, the term $\frac{1}{2} \sum_i \sum_{i \neq j} J_{ij}$ has to be subtracted from $\sum_i \varepsilon_i$.

Ionization energy

- If an electron labeled *k* from the orbital ϕ_k is removed to infinity, the atoms becomes ionized. If we ignore any change of the orbital functions the energy of the ion is then given by

$$E_{ion} = \sum_{i\neq k} E'_k - \frac{1}{2}\sum_{i\neq k}\sum_{j\neq k, i\neq j} \int\int \phi_i\phi_j \frac{e'^2}{r_{ij}} \phi_i\phi_j d\tau_i d\tau_j$$

$$E_{ion} = E - \int \phi_k \left| -\frac{1}{2m_e}\nabla_k^2 - \frac{Ze'^2}{r_k} \right| \phi_k d\tau_k - \sum_{j\neq k} \int\int \phi_k\phi_j \frac{e'^2}{r_{jk}} \phi_k\phi_j d\tau_k d\tau_j$$

Thus we have the relation

$$-\varepsilon'_k = \varepsilon_{ion} - \varepsilon$$

This means that -$\varepsilon_k{}'$ represents the ionization energy of the atom in which an electron is removed from the orbital ϕ_k. This method has been applied by Hartree to several atoms and ions.

Electron Spin

To explain this *fine structure* of atomic spectra, Uhlenbeck and Goudsmit proposed in 1925 that the electron has an *intrinsic* (built-in) angular momentum in addition to the orbital angular momentum due to its motion about the nucleus. If we picture the electron as a sphere of charge spinning about one of its diameters, we can see how such an intrinsic angular momentum can arise. Hence we have the term *spin angular momentum* or, more simply, *spin.*

However, electron "spin" is not a classical effect, and the picture of an electron rotating about an axis has no physical reality. The intrinsic angular momentum is real, but no easily visualizable model can explain its origin properly. We cannot hope to understand microscopic particles based on models taken from our experience in the macroscopic world. Other elementary particles besides the electron have spin angular momentum.

We have learned that each physical property has its corresponding linear Hermitian operator in quantum mechanics. For such properties as orbital angular momentum, we can construct the quantum-mechanical operator from the classical expression by replacing *Px• Py• Pz* by the appropriate operators. The inherent spin angular momentum of a microscopic particle has no analog in classical mechanics, so we cannot use this method to construct operators for spin. For our purposes, we shall simply use symbols for the spin operators, without giving an explicit form for them.

Analogous to the orbital angular-momentum operators *L^2, ix, Ly, Lz,* we have the spin angular-momentum operators S^2, *S x*• *SY' S* z• Which are postulated to be linear and Hermitian. S^2 is the operator for the square of the magnitude of the total spin angular momentum of a particle. *S* z is the operator for the *z* component of the particle's spin angular momentum. We have

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \qquad (10.1)$$

We postulate that the spin angular-momentum operators obey the same commutation relations as the orbital angular-momentum operators. Analogous to *[Lx, Ly] = ifiLz, [Ly, Lz] = ifiLx, [Lz, Lx] = ifiLy*, we have

$$[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z, \qquad [\hat{S}_y, \hat{S}_z] = i\hbar\hat{S}_x, \qquad [\hat{S}_z, \hat{S}_x] = i\hbar\hat{S}_y \tag{10.2}$$

From (10.1) and (10.2),

$$[\hat{S}^2, \hat{S}_x] = [\hat{S}^2, \hat{S}_y] = [\hat{S}^2, \hat{S}_z] = 0 \tag{10.3}$$

The eigenvalues of S^2 are

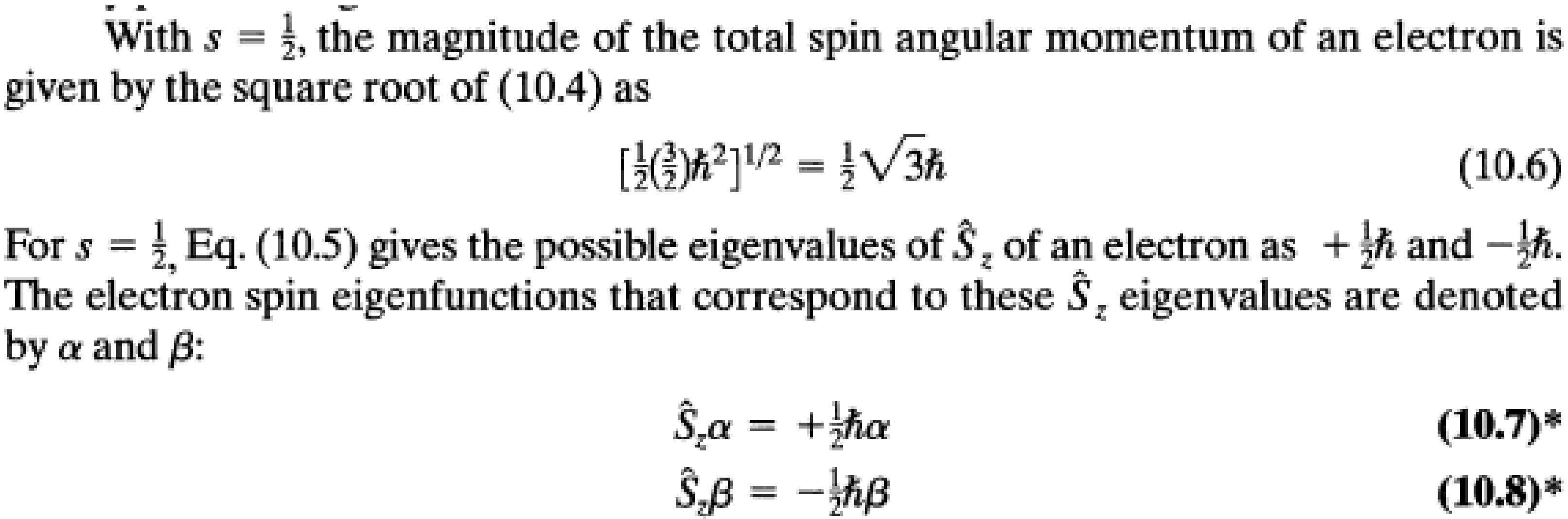
$$s(s+1)\hbar^2, \qquad s = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, \ldots \tag*{\textbf{(10.4)}}$$

and the eigenvalues of S_z are

$$m_s\hbar, \qquad m_s = -s, -s+1, \ldots, s-1, s \tag*{\textbf{(10.5)}}$$

The quantum number *s* is called the *spin* of the particle. Although nothing in Section 5.4 restricts electrons to a single value for *s,* experiment shows that all electrons do have a single value for *s,* namely, $s = 1/2$. Protons and neutrons also have $s = 1/2$. Pions have $s = 0$. Photons have $s = 1$.

However, Eq. (10.5) does not hold for photons. Photons travel at speed *c* in vacuum. Because of their relativistic nature, it turns out that photons can have either $m_s = +1$ or $m_s = -1$, but not $m_s = 0$. These two m_s values correspond to left circularly polarized and right circularly polarized light.



With $s = \frac{1}{2}$, the magnitude of the total spin angular momentum of an electron is given by the square root of (10.4) as

$$[\tfrac{1}{2}(\tfrac{3}{2})\hbar^2]^{1/2} = \tfrac{1}{2}\sqrt{3}\hbar \qquad (10.6)$$

For $s = \frac{1}{2}$, Eq. (10.5) gives the possible eigenvalues of $\hat{S}_z$ of an electron as $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$. The electron spin eigenfunctions that correspond to these $\hat{S}_z$ eigenvalues are denoted by α and β:

$$\hat{S}_z\alpha = +\tfrac{1}{2}\hbar\alpha \qquad \textbf{(10.7)*}$$

$$\hat{S}_z\beta = -\tfrac{1}{2}\hbar\beta \qquad \textbf{(10.8)*}$$

Since $\hat{S}_z$ commutes with $\hat{S}^2$, we can take the eigenfunctions of $\hat{S}_z$ to be eigenfunctions of $\hat{S}^2$ also, with the eigenvalue given by (10.4) with $s = \frac{1}{2}$:

$$\hat{S}^2\alpha = \tfrac{3}{4}\hbar^2\alpha, \qquad \hat{S}^2\beta = \tfrac{3}{4}\hbar^2\beta \tag{10.9}$$

$\hat{S}_z$ does not commute with $\hat{S}_x$ or $\hat{S}_y$, so α and β are not eigenfunctions of these operators. The terms *spin up* and *spin down* refer to $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$, respectively. See Fig. 10.1. We shall later show that the two possibilities for the quantum number m_s give the doubling of lines in the spectra of the alkali metals.

FIGURE 10.1 Possible orientations of the electron spin vector with respect to the z axis. In each case, **S** lies on the surface of a cone whose axis is the z axis.

The wave functions we have dealt with previously are functions of the spatial coordinates of the particle: $\psi = \psi(x, y, z)$. We might ask: What is the variable for the spin eigenfunctions α and β? Sometimes one talks of a spin coordinate ω, without really specifying what this coordinate is. Most often, one takes the spin quantum number m_s as being the variable on which the spin eigenfunctions depend. This procedure is quite unusual as compared with the spatial wave functions; but because we have only two possible electronic spin eigenfunctions and eigenvalues, this is a convenient choice. We have

$$\alpha = \alpha(m_s), \qquad \beta = \beta(m_s) \tag{10.10}$$