Multiparticle systems

• Previous part: principles of quantum mechanics applied for systems with a single particle

• Atoms and molceules: simultaneous presence of several particles

• In a system of N particles, these particles do not have individual states, the system can only be characterized with a joint wave function:

$$\Psi(x_1,y_1,z_1,m_{s1},x_2,y_2,z_2,m_{s2},\ldots,x_N,y_N,z_N,m_{sN},t)$$

spin coordinates

or $\Psi(1,2,\ldots,N,t)$

Multiparticle systems

• The probability that the individual particles will be found in the region with volume $\mathrm{d}V = \mathrm{d}V_1\cdot\mathrm{d}V_2\cdot\ldots\cdot\mathrm{d}V_N$ around the coordinates:

$$\Psi^*(1,2,\ldots,N,t)\Psi(1,2,\ldots,N,t)\mathrm{d}V$$

• The state equation (Schrödinger equation):

$$-\frac{\hbar}{\mathrm{i}}\frac{\partial\Psi}{\partial t} = -\sum_{j=1}^{N}\frac{\hbar^2}{2\mu_j}\Delta_j\Psi + V\Psi$$

Laplace operator: derivation with respect to spatial coordinate j:

$$\Delta_j = \frac{\partial^2}{\partial x_j^2}+\frac{\partial^2}{\partial y_j^2}+\frac{\partial^2}{\partial z_j^2}$$

the total interaction energy of particles

Multiparticle systems

• Solving the Schrödinger equation of multiparticle systems is often very complicated

• Approximation methods are necessary
e.g. principle of variation

• The appropriate Hamilton operator:

$$H = -\sum_{j=1}^{N}\frac{\hbar^2}{2\mu_j}\Delta_j + V$$

$$E_0 = \frac{\int\Psi_0^* H\Psi_0\mathrm{d}V}{\int\Psi_0^*\Psi_0\mathrm{d}V}$$

$$E = \frac{\int\Psi^* H\Psi\mathrm{d}V}{\int\Psi^*\Psi\mathrm{d}V}$$

• The stationary Schrödinger equation:

$$-\sum_{j=1}^{N}\frac{\hbar^2}{2\mu_j}\Delta_j\Psi + V\Psi = E\Psi$$

The structure of atoms

• Elementary particles in atoms:

	proton	neutron	electron
mass (kg)	$1.67262\cdot10^{-27}$	$1.67493\cdot10^{-27}$	$9.10939\cdot10^{-31}$
charge (C)	$1.60218\cdot10^{-19}$ (e)	0	$-1.60218\cdot10^{-19}$ ($-e$)

• Size of the nucleus: 10^{-15} m (nuclear physics, nuclear chemistry)
• Electron cloud (quantum mechanics:
– the nucleus is considered to be a point charge
– the nucleus is practically stationary relative to the center of mass of the atom)

Hydrogen-like particles

e.g.: H, He^+, Li^{2+}, Be^{3+}, U^{91+}

• nucleus with Ze charge
• a single electron

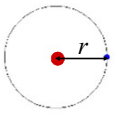
• The interaction between the nucleus and the electron is given by the Coulomb potential:

$$V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$

vacuum permittivity ($8.85419\cdot10^{-12}\ \mathrm{J^{-1}C^2m^{-1}}$)

• The stationary Schrödinger equation for the movement of the electron:

$$-\frac{\hbar^2}{2\mu}\Delta\Psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\Psi = E\Psi$$

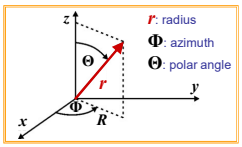


Hydrogen-like particles

$n = 1,2,3,\ldots$

$l = 0,1,2,\ldots,(n-1)$

$m = -l, -(l-1),\ldots,0,\ldots,(l-1),l$



• The stationary Schrödinger equation for the movement of the electron:

$$-\frac{\hbar^2}{2\mu}\Delta\Psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\Psi = E\Psi$$

• In a spherical coordinate system:

$$E_n = -\frac{1}{(4\pi\varepsilon_0)^2}\frac{\mu Z^2 e^4}{2n^2\hbar^2} \quad \text{and} \quad \Psi_{n,l,m} = R_{n,l}(r)Y_{l,m}(\Theta,\Phi)$$

Hydrogen-like particles

$n = 1,2,3,\ldots$

$l = 0,1,2,\ldots,(n-1)$

$m = -l, -(l-1),\ldots,0,\ldots,(l-1),l$

$$N_{n,l} = \left[\frac{(n-l-1)!}{2n[(n+l)!]^3}\left(\frac{2Z}{na_0}\right)^{2l+3}\right]^{1/2}$$

$$R_{n,l}(r) = -N_{n,l} r^l \exp\left(-\frac{Zr}{na_0}\right) L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)$$

radial wave function

$$E_n = -\frac{1}{(4\pi\varepsilon_0)^2}\frac{\mu Z^2 e^4}{2n^2\hbar^2} \quad \text{and} \quad \Psi_{n,l,m} = R_{n,l}(r)Y_{l,m}(\Theta,\Phi)$$

Hydrogen-like particles

$n = 1,2,3,\ldots$

$l = 0,1,2,\ldots,(n-1)$

$m = -l, -(l-1),\ldots,0,\ldots,(l-1),l$

$$L_q^s(\xi) = \frac{d^s}{d\xi^s}\left[e^{\xi}\frac{d^q}{d\xi^q}\left(\xi^q e^{-\xi}\right)\right]$$

associated Laguerre polynomial

$$R_{n,l}(r) = -N_{n,l} r^l \exp\left(-\frac{Zr}{na_0}\right) L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)$$

radial wave function

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Hydrogen-like particles

$n = 1,2,3,\ldots$

$l = 0,1,2,\ldots,(n-1)$

$m = -l, -(l-1),\ldots,0,\ldots,(l-1),l$

Bohr radius: $a_0 = \dfrac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$

$$R_{n,l}(r) = -N_{n,l} r^l \exp\left(-\frac{Zr}{na_0}\right) L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)$$

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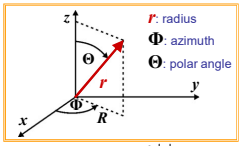


$$P_l^{|m|}(\xi) = \left(2^l l!\right)^{-1}\left(1-\xi^2\right)^{|m|/2}\frac{d^{l+|m|}}{d\xi^{l+|m|}}\left(\xi^2-1\right)^l$$

associated Legendre polynomial

$$Y_{l,m} = N_{l,m} P_l^{|m|}(\cos\Theta)e^{im\Phi}$$

same as the wave function of a particle moving on the surface of a sphere

angular wave function

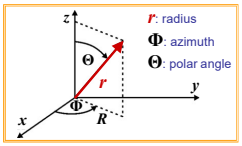
$$E_n = -\frac{1}{(4\pi\varepsilon_0)^2}\frac{\mu Z^2 e^4}{2n^2\hbar^2} \quad \text{and} \quad \Psi_{n,l,m} = R_{n,l}(r)Y_{l,m}(\Theta,\Phi)$$

Hydrogen-like particles

$n = 1,2,3,\ldots$

$l = 0,1,2,\ldots,(n-1)$

$m = -l, -(l-1),\ldots,0,\ldots,(l-1),l$



$$N_{l,m} = \left[\frac{(l-|m|)!(2l+1)}{4\pi(l-|m|)!}\right]^{1/2}$$

normalization factor

$$Y_{l,m} = N_{l,m} P_l^{|m|}(\cos\Theta)e^{im\Phi}$$

same as the wave function of a particle moving on the surface of a sphere

angular wave function

$$E_n = -\frac{1}{(4\pi\varepsilon_0)^2}\frac{\mu Z^2 e^4}{2n^2\hbar^2} \quad \text{and} \quad \Psi_{n,l,m} = R_{n,l}(r)Y_{l,m}(\Theta,\Phi)$$

Hydrogen-like particles

• Conventions for designating $\Psi_{n,l,m}$ wave functions:

$n = 1,2,3,4,\ldots$	the number itself
$l = 0,1,2,3,\ldots$	$s,p,d,f,\ldots$
$m = -l, -(l-1),\ldots,0,\ldots,(l-1),l$	subscript (if needed)

$$E_n = -\frac{1}{(4\pi\varepsilon_0)^2}\frac{\mu Z^2 e^4}{2n^2\hbar^2} \quad \text{and} \quad \Psi_{n,l,m} = R_{n,l}(r)Y_{l,m}(\Theta,\Phi)$$

Hydrogen-like particles

• Radial wave function of hydrogen-like particles:

$$R_{n,l}(r) = -N_{n,l} r^l \exp\left(-\frac{Zr}{na_0}\right) L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)$$

radial wave function

orbital	radial wave function
$1s$	$R_{1,0} = 2(Z/a_0)^{3/2}\exp(-Zr/a_0)$
$2s$	$R_{2,0} = \left[(Z/a_0)^{3/2}(2 - Zr/a_0)\exp(-Zr/2a_0)\right]/2^{3/2}$
$2p$	$R_{2,1} = \left[(Z/a_0)^{3/2}(Zr/a_0)\exp(-Zr/2a_0)\right]/(2\cdot 6^{1/2})$
$3s$	$R_{3,0} = \left[2(Z/a_0)^{3/2}(27 - 18Zr/a_0 + 2(Zr/a_0)^2)\exp(-Zr/3a_0)\right]/(81\cdot 3^{1/2})$
$3p$	$R_{3,1} = \left[4(Z/a_0)^{3/2}(6Zr/a_0 - (Zr/a_0)^2)\exp(-Zr/3a_0)\right]/(81\cdot 6^{1/2})$
$3d$	$R_{3,2} = \left[4(Z/a_0)^{3/2}(Zr/a_0)^2\exp(-Zr/3a_0)\right]/(81\cdot 3^{1/2})$

Hydrogen-like particles

orbital	angular wave function
s	$Y_{0,0} = (1/4\pi)^{1/2}$
p_z	$Y_{1,0} = (3/4\pi)^{1/2}\cos\Theta$
p_x	$Y_{1,\cos\Phi} = (6/8\pi)^{1/2}\sin\Theta\cos\Phi$
p_y	$Y_{1,\sin\Phi} = (6/8\pi)^{1/2}\sin\Theta\sin\Phi$
d_{z^2}	$Y_{2,0} = (5/16\pi)^{1/2}(3\cos^2\Theta - 1)$
d_{xz}	$Y_{2,\cos\Phi} = (30/8\pi)^{1/2}\cos\Theta\sin\Theta\cos\Phi$
d_{yz}	$Y_{2,\sin\Phi} = (30/8\pi)^{1/2}\cos\Theta\sin\Theta\sin\Phi$
$d_{x^2-y^2}$	$Y_{2,\cos 2\Phi} = (30/32\pi)^{1/2}\sin^2\Theta\cos 2\Phi$
d_{xy}	$Y_{2,\sin 2\Phi} = (30/32\pi)^{1/2}\sin^2\Theta\sin 2\Phi$

To obtain real atomic orbitals the real combinations of complex $Y_{l,m}$ functions, (*i.e.* $Y_{l,\cos m\Phi}$ and $Y_{l,\sin m\Phi}$) are used:

Hydrogen-like particles

orbital	angular wave function
s	$Y_{0,0} = (1/4\pi)^{1/2}$
p_z	$Y_{1,0} = (3/4\pi)^{1/2}\cos\Theta$
p_x	$Y_{1,\cos\Phi} = (6/8\pi)^{1/2}\sin\Theta\cos\Phi$
p_y	$Y_{1,\sin\Phi} = (6/8\pi)^{1/2}\sin\Theta\sin\Phi$
d_{z^2}	$Y_{2,0} = (5/16\pi)^{1/2}(3\cos^2\Theta - 1)$
d_{xz}	$Y_{2,\cos\Phi} = (30/8\pi)^{1/2}\cos\Theta\sin\Theta\cos\Phi$
d_{yz}	$Y_{2,\sin\Phi} = (30/8\pi)^{1/2}\cos\Theta\sin\Theta\sin\Phi$
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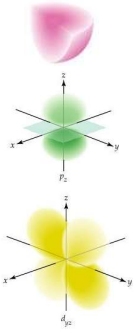
d_{xy}	$Y_{2,\sin 2\Phi} = (30/32\pi)^{1/2}\sin^2\Theta\sin 2\Phi$



Hydrogen-like particles

orbital	angular wave function
s	$Y_{0,0} = (1/4\pi)^{1/2}$
p_z	$Y_{1,0} = (3/4\pi)^{1/2}\cos\Theta$
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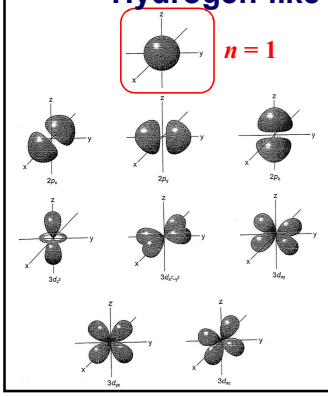
d_{xy}	$Y_{2,\sin 2\Phi} = (30/32\pi)^{1/2}\sin^2\Theta\sin 2\Phi$

For a single energy value, there are

$$\sum_{l=0}^{n-1}(2l+1) = n^2$$

wave functions (degree of degeneration)

Hydrogen-like particles



$n = 1$

For a single energy value, there are

$$\sum_{l=0}^{n-1}(2l+1) = n^2$$

wave functions (degree of degeneration)

Hydrogen-like particles

• The radial density function is suitable for characterizing the electron:

$$P_{n,l}(r) = r^2\left|R_{n,l}(r)\right|^2$$

(The probability that the electron with quantum numbers n,l is found within the spherical shell of radius r and thickness $\mathrm{d}r$)

• The probability of finding the electron in the sphere with radius R is:

$$w = \int_0^R P_{n,l}(r)\,\mathrm{d}r$$

For the $1s$ orbital:

$$P_{1,0}(r) = r^2 4\left(\frac{Z}{a_0}\right)^3 \mathrm{e}^{-2Zr/a_0} \Rightarrow r_{\max} = \frac{a_0}{Z}$$

H atom: $r_{\max} = a_0$

Hydrogen-like particles

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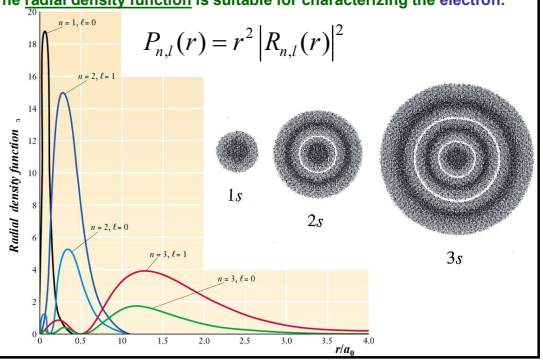


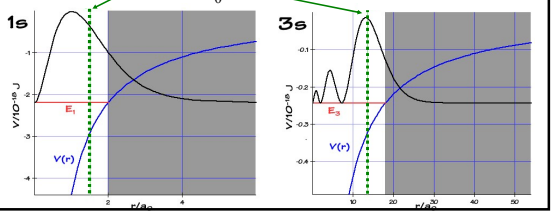
Hydrogen-like particles

• The radial density function is suitable for characterizing the electron:

$$P_{n,l}(r) = r^2 \left|R_{n,l}(r)\right|^2$$

and the average distance from the nucleus:

$$\bar{r}_{n,l} = \int_0^\infty P_{n,l}(r) r \mathrm{d}r$$



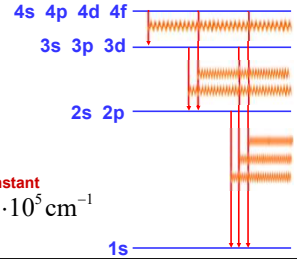
Hydrogen-like particles

Spectra of hydrogen-like particles:

• The photon with c Speed emitted during the $n_2 \rightarrow n_1$ (where $n_2 > n_1$) electron transition has an energy that is identical to the energy difference between the initial and final states.

•The wavelength of the photon:

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$



Rydberg constant

$$R_\infty = \frac{\mu Z^2 e^4}{8\varepsilon_0^2 h^3 c} = 1.09737 \cdot 10^5 \,\mathrm{cm}^{-1}$$

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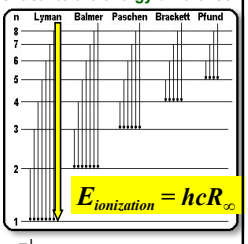

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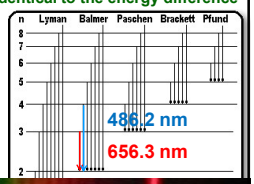

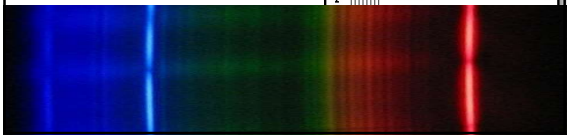

Hydrogen-like particles

• The absolute value of the angular momentum arising from the movement of the electron around the nucleus (orbital angular momentum):

$$|\mathrm{L}| = \sqrt{l(l+1)}\hbar$$

the component of the angular momentum in direction z:

$$L_z = m\hbar$$

• Experience shows that electrons have angular momentum even if they do not move around a nucleus (intrinsic angular momentum or spin), this is an inherent property of particles.

$$|\mathrm{S}| = \sqrt{s(s+1)}\hbar \text{ and } S_z = m_s\hbar$$

where $s = \frac{1}{2}$ (spin quantum number)

$m_s = \pm\frac{1}{2}$ (spin states)

α and β (spin functions)

The total wave function of the electron (including spin) :

$$\Psi_{n,l,m,\frac{1}{2}} = \Psi_{n,l,m}\alpha$$

$$\Psi_{n,l,m,-\frac{1}{2}} = \Psi_{n,l,m}\beta$$

Hydrogen-like particles

For a single energy value, there are

$$2\sum_{l=0}^{n-1}(2l+1)=2n^2$$

wave functions (degree of degeneration)

$|\mathrm{S}|=\sqrt{s(s+1)}\hbar$ and $S_z=m_s\hbar$

where $s=\frac{1}{2}$ (spin quantum number)

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The total wave function of the electron (including spin) :

$$\Psi_{n,l,m,\frac{1}{2}}=\Psi_{n,l,m}\alpha$$

$$\Psi_{n,l,m,-\frac{1}{2}}=\Psi_{n,l,m}\beta$$

Hydrogen-like particles

- It is not only electrons that have spin
- Fermions have half-integer spins, Bosons have integer spins.

Satjendra Nath Bose (1894-1974)

photon
α-particle

electron
proton
neutron

Enrico Fermi (1901-1954)

$m_s=-s,-(s-1),\ldots,(s-1),s$ (spin states)

Multielectron particles

- The stationary Schrödinger equation of the system:

$$\left[-\frac{\hbar^2}{2\mu}\sum_{i=1}^{N}\Delta_i+\frac{e^2}{4\pi\varepsilon_0}\left(-\sum_{i=1}^{N}\frac{Z}{r_i}+\sum_{i=1}^{N}\sum_{\substack{j=1\\i<j}}^{N}\frac{1}{r_{ij}}\right)\right]\Psi=E\Psi$$

Z: atomic number

N: number of electrons

distance between the electron and the nucleus

distance between two electrons

- Solution is only possible by approximation.
- A rather complicated variational probe function (*i.e.* one with many parameters) is needed to obtain good approximations in simple systems.
- The independent particle approach make it possible to handle the electron structure in a way easy to visualize.

Multielectron particles

- Assume that the interaction with the N electrons with each other is negligible.
- Electrons are individually characterized by N independent Schrödinger equations.
- *E.g.* for electron i then:

$$\left[-\frac{\hbar^2}{2\mu}\sum_{i=1}^{N}\Delta_i+\frac{e^2}{4\pi\varepsilon_0}\left(-\frac{Z}{r_i}\right)\right]\Psi_i(i)=E_i\Psi_i(i)$$

(A suitable number of electrons placed on the orbitals of a hydrogen-like atom.)

- The wave function of the electron characterized by quantum numbers (n,l,m,m_s):

$$\Psi_{n,l,m,m_s}=\varphi_{n,m,l}\sigma_{m_s}$$

electron orbital (spin orbital)

atomic orbital

spin function

Multielectron particles

The simplest approach: independent particles

- It is impossible to have two electrons with the same four quantum numbers within a single atom.
- An atomic orbital can host only 2 electrons (Pauli's exclusion principle).

$n=1,2,3,4,\ldots$	$K,L,M,N,\ldots$
$l=0,1,2,3,\ldots$	$s,p,d,f,\ldots$

Shell

Subshell

Electron configuration: shows how many electron are on individual subshells (*e.g.*: Ne: $1s^22s^22p^6$)

- The total wave function of the atom is the product of the electron wave functions: $\Psi(1,2,\ldots,N)=\Psi_1(1)\Psi_2(2)\ldots\Psi_N(N)$
- The total energy is the sum of the individual energies:

$$E=E_1+E_2+\ldots+E_N$$

- Energy minimum: the ground state is the one with the lowest energy.

Multielectron particles

Approximation using independent particles:
Hartree's SCF (Self-Consistent Field) method

- The multiparticle Schrödinger equation is separated into individual particles, but the interaction between the particles is considered.

$\Psi(1,2,\ldots,N)=\Psi_1(1)\Psi_2(2)\ldots\Psi_N(N)$ (the same as in the previous case)

$$\left[-\frac{\hbar^2}{2\mu}\Delta_i+\frac{e^2}{4\pi\varepsilon_0}\left(-\frac{Z}{r_i}\right)+v_i(r_i)\right]\Psi_i(i)=E_i\Psi_i(i)$$

potential energy arising form the interaction of electron i with all other electrons

$$v_i(r_i)=\frac{e^2}{4\pi\varepsilon_0}\sum_{\substack{j=1\\j\neq i}}^{N}\int\frac{|\Psi_j(j)|^2}{r_{ij}}\mathrm{d}V_j \quad \text{where } i=1,2,\ldots,N$$

Multielectron particles

Approximation using independent particles:
Hartree's SCF (Self-Consistent Field) method

- Average charge density arising from the movement of electron j:

$$-e\left|\Psi_j(j)\right|^2$$

- Divide this charge cloud into small part with volume $\mathrm{d}V_j$.
- In such a part, the point charge is $-e\left|\Psi_j(j)\right|^2\mathrm{d}V_j$.
- For electron i, this contributes $e^2\left|\Psi_j(j)\right|^2/(4\pi\varepsilon_0 r_{ij})$ to the electrostatic potential.
- The total potential energy arising from the charge of electron j is calculated as the sum/integral of this small point charges.

$$v_i(r_i)=\frac{e^2}{4\pi\varepsilon_0}\sum_{\substack{j=1\\ j\neq i}}^{N}\int\frac{\left|\Psi_j(j)\right|^2}{r_{ij}}\mathrm{d}V_j \quad \text{where } i=1,2,\ldots,N$$

Multielectron particles

Approximation using independent particles:
Hartree's SCF (Self-Consistent Field) method

The Schrödinger equation is often solved iteratively:

1. Initially, the wave functions $\Psi_1, \ldots, \Psi_N$ hare approximated by the orbitals of hydrogen-like atoms,
2. the potentials $v_i(r_i)$ are calculated and the Scrödinger equation is solved.
- …
- Step 2 is repeated until one iteration step does not change the $\Psi_1, \ldots, \Psi_N$ functions any more.

$$\Psi(1,2,\ldots,N)=\Psi_1(1)\Psi_2(2)\ldots\Psi_N(N)$$
$$E=\int\Psi^*H\Psi\,\mathrm{d}V$$

Multielectron particles

Approximation using independent particles:
Hartree–Fock SCF method

- The total wave function of an atom is given in the form of a determinant,
- tries to account for the equivalence of electrons.
- The wave function of particles with half-integer spin can only be antisymmetric (this is Pauli's exclusion principle in a general form):

$$\Psi(1,2,\ldots,N)=-\Psi(2,1,\ldots,N)$$

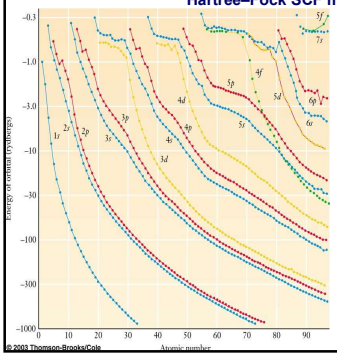
Slater determinants:

$$\Psi(1,2,\ldots,N)=c\begin{vmatrix}\Psi_1(1) & \Psi_2(1) & \cdots & \Psi_N(1)\\ \Psi_1(2) & \Psi_2(2) & \cdots & \Psi_N(2)\\ \vdots & \vdots & & \vdots\\ \Psi_1(N) & \Psi_2(N) & \cdots & \Psi_N(N)\end{vmatrix}$$

- The wave function of a closed shell system (noble gas atom, alkali metal ions) consist of a single Slater determinant.

Multielectron particles

Approximation using independent particles:
Hartree–Fock SCF method



- Calculations can be carried out for every atom and ion,
- the relative error of the total energy is about 1%,
- this is in the order of the energy changes of the valence shell,

→ ionization and excitation energies obtained by this method are not very accurate.