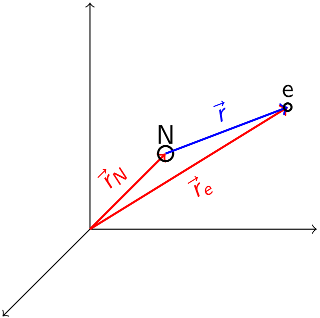
Outlines of Quantum Physics

1. Wave-Particle Duality

2. The Schrödinger Equation

3. The Hydrogen Atom
   - Schrödinger Eq. of the Hydrogen Atom
   - Noninteracting Particles and Separation of Variables
   - The One-Particle Central Force Problem
   - Energy levels of the Hydrogenlike atom
   - Hydrogenlike-Atom Wave Functions

Schrödinger Eq. of the Hydrogen Atom



氢原子或类氢原子:

$$H = -\frac{\hbar^2}{2M_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{Ze'^2}{r}$$

其中 $\vec{r} = \vec{r}_e - \vec{r}_N$

$e'^2 = e^2/4\pi\epsilon_0$

Noninteracting Particles and Separation of Variables

$$\hat{H} = \hat{H}_1 + \hat{H}_2, \qquad (\hat{H}_1 + \hat{H}_2)\Psi(q_1, q_2) = E\Psi(q_1, q_2)$$

其中$\hat{H}_1$ 只和粒子 1 有关；$\hat{H}_2$ 只和粒子 2 有关；

分离变量法，假设 $\Psi(q_1, q_2) = G_1(q_1)G_2(q_2)$:

$$\begin{aligned}
\hat{H}_1 G_1(q_1)G_2(q_2) + \hat{H}_2 G_1(q_1)G_2(q_2) &= EG_1(q_1)G_2(q_2)\\
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\end{aligned}$$

Left part must be a constant,

$$\hat{H}_1 G_1(q_1) = E_1 G_1(q_1), \qquad \hat{H}_2 G_2(q_2) = E_2 G_2(q_2)$$

$$E_1 + E_2 = E$$

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Noninteracting Particles and Separation of Variables

可推广到 n 个独立 “粒子” 问题：

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \cdots + \hat{H}_n$$
$$\Psi(q_1, q_2, \cdots, q_n) = G_1(q_1)G_2(q_2)\cdots G_n(q_n)$$
$$E = E_1 + E_2 + \cdots + E_n$$
$$\hat{H}_i G_i = E_i G_i, \qquad i = 1, 2, \cdots, n$$

Reduction of the Two-Particle Problem to Two One-Particle Problem

质心坐标系方法:

$$\vec{R}(X,Y,Z) = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1+m_2}$$

$$\vec{r}(x,y,z) = \vec{r}_1 - \vec{r}_2$$

$$M = m_1 + m_2; \qquad \mu = \frac{m_1 m_2}{m_1+m_2}$$

$$\nabla_R^2 = \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}$$

$$\nabla_r^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

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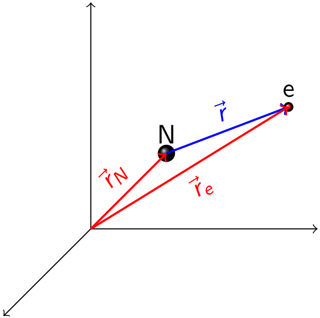

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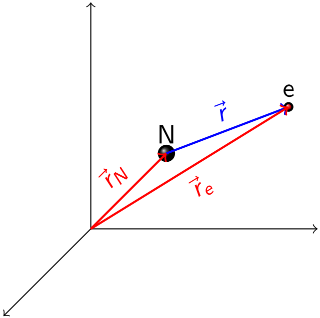

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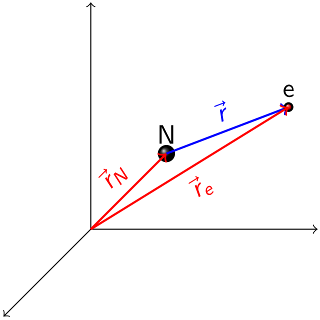

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则 S.eq 可化为:

$$[\underline{-\frac{\hbar^2}{2M}\nabla_R^2}\underline{-\frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)}]\Psi = E_{total}\Psi$$

分离变量法,

$$\begin{aligned}\Psi(\vec{R},\vec{r}) &= \Psi_c(\vec{R})\Psi_e(\vec{r}) \\ -\frac{\hbar^2}{2M}\nabla_R^2\Psi_c(\vec{R}) &= E_c\Psi_c(\vec{R}) \\ [-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)]\Psi_e(\vec{r}) &= E\Psi_e(\vec{r}) \\ E_{total} &= E_c + E\end{aligned}$$

即分解成质心的平动和内部运动。
这个方法是精确的,但无法推广到多体问题。

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三维中心力场

$$[-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)]\Psi(\vec{r}) = E\Psi(\vec{r})$$

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}],$$

$$\hat{L}^2 = -\hbar^2[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}],$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi},$$

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分离变量法求解

$$[-\frac{\hbar^2}{2\mu r}\frac{\partial^2}{\partial r^2}r + V(r) + \frac{1}{2\mu r^2}\hat{L}^2]\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi)$$

可以分解为：

$$\Psi = R(r)Y(\theta,\phi)$$

角向方程

$$\hat{L}^2 Y(\theta,\phi) = \beta\hbar^2 Y(\theta,\phi)$$

径向方程

$$[\frac{1}{r}\frac{d^2}{dr^2}r + 2\frac{\mu}{\hbar^2}(E-V) - \frac{\beta}{r^2}]R_\ell(r) = 0$$

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角向方程，球谐函数

$$\hat{L}^2 Y(\theta,\phi) = \beta\hbar^2 Y(\theta,\phi)$$

其解

$$Y_{\ell m}(\theta,\phi) = (-1)^{\frac{m+|m|}{2}}\sqrt{\frac{(2\ell+1)(\ell-|m|)!}{4\pi(\ell+|m|)!}}P_\ell^{|m|}(cos\theta)\frac{1}{\sqrt{2\pi}}e^{im\phi}$$

$$\hat{L}^2 Y_{\ell m}(\theta,\phi) = \ell(\ell+1)\hbar^2 Y_{\ell m}(\theta,\phi)$$

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta Y^*_{\ell m} Y_{\ell' m'} \sin\theta = \delta_{\ell\ell'}\delta_{mm'}$$

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Radial Function and Energy levels

$$\frac{\hbar^2}{2\mu}(R_\ell'' + \frac{2}{r}R_\ell') + V(r)R_\ell + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}R_\ell = ER_\ell(r)$$

一般中心力场中，其解：

$$R = R_{n\ell}(r), \quad \int_0^\infty R_{n\ell}R_{n'\ell}r^2 dr = \delta_{nn'}$$

$$E = E_{n\ell}$$

能量本征态一般是 $2\ell+1$ 重简并，与 m 量子数无关。
对于类氢离子 $V(r) = Ze'^2/r$，其解

$$\begin{aligned} R_{n\ell}(r) &= N_{n\ell}e^{-\frac{Zr}{na}}(\frac{2Z}{na}r)^\ell L_{n+\ell}^{2\ell+1}(\frac{2Z}{na}r) \\ a &= \hbar^2/\mu e'^2 = \frac{\hbar}{\alpha\mu c} \end{aligned}$$

$e'^2 = e^2/4\pi\epsilon_0$

Radial Function and Energy levels

$$\frac{\hbar^2}{2\mu}(R_\ell'' + \frac{2}{r}R_\ell') + V(r)R_\ell + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}R_\ell = ER_\ell(r)$$

一般中心力场中，其解：

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$$a = \hbar^2/\mu e'^2 = \frac{\hbar}{\alpha\mu c}$$

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Energy levels of hydrogenlike atom

$$
\begin{aligned}
\Psi_{n\ell m} &= R_{n\ell}(r)Y_{\ell m}(\theta,\phi) \\
H\Psi_{n\ell m} &= E_n\Psi_{n\ell m} \\
E_n &= -\frac{Z^2}{2n^2}\cdot\frac{\mu e'^4}{\hbar^2} = -\frac{Z^2}{2n^2}\cdot\mu c^2\alpha^2 \\
L^2\Psi_{n\ell m} &= \ell(\ell+1)\hbar^2\Psi_{n\ell m} \\
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\ell &= 0,1,2,3\cdots,n-1 \\
m &= 0,\pm1,\pm2,\cdots,\pm\ell
\end{aligned}
$$

- $\ell = 0$(sharp), 1(principle), 2(diffuse), 3(fundamental), $\cdots$
- $hcR_\infty = \frac{1}{2}\alpha^2 m_e c^2 \approx 13.6\text{eV}$, $a_0 = \frac{\hbar}{\alpha m_e c} \approx 0.529\text{Å}$, $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137}$
- $R_\infty = 109\ 737.315\ 681\ 60(21)\ \text{cm}^{-1}$, $R_M = R_\infty\frac{M}{m_e+M}$

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Hydrogenlike-Atom Wave Functions

$$\Psi_{n\ell m} = R_{n\ell}(r) Y_{\ell m}(\theta, \phi)$$

$$R_{n\ell}(r) = \sqrt{\left(\frac{2Z}{na}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}}\, e^{-\frac{Zr}{na}} \left(\frac{2Z}{na} r\right)^\ell L_{n+\ell}^{2\ell+1}\left(\frac{2Z}{na} r\right)$$

$$Y_{\ell m}(\theta, \phi) = (-1)^{\frac{m+|m|}{2}} \sqrt{\frac{(2\ell+1)(\ell-|m|)!}{4\pi(\ell+|m|)!}}\, P_\ell^{|m|}(\cos\theta) \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

where $a \equiv 4\pi\epsilon_0\hbar^2/\mu e^2$

Radial Hydrogenic Wavefunction $R_{n\ell}$

$$R_{1s} = (\frac{Z}{a})^{3/2} 2e^{-\rho}$$

$$R_{2s} = (\frac{Z}{2a})^{3/2} 2(1-\rho)e^{-\rho}$$

$$R_{2p} = (\frac{Z}{2a})^{3/2} \frac{2}{\sqrt{3}}\rho e^{-\rho}$$

$$R_{3s} = (\frac{Z}{3a})^{3/2} 2(1-2\rho+\frac{2}{3}\rho^2)e^{-\rho}$$

$$R_{3p} = (\frac{Z}{3a})^{3/2} \frac{4\sqrt{2}}{3}\rho(1-\rho/2)e^{-\rho}$$

$$R_{3d} = (\frac{Z}{3a})^{3/2} \frac{2\sqrt{2}}{3\sqrt{5}}\rho^2 e^{-\rho}$$

$$a \equiv 4\pi\epsilon_0\hbar^2/\mu e^2$$

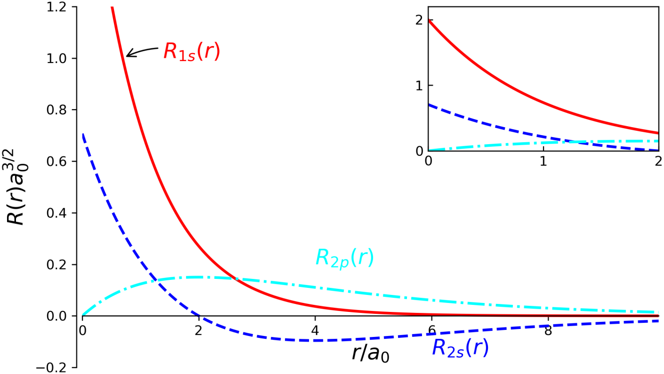
$$\rho = \frac{Zr}{na}$$

$\ell = 0$ 时，在 $r = 0$ 原点处:
$|\Psi_{n,\ell=0}(0)|^2 = \frac{1}{\pi}(\frac{Z}{na})^3$

$$\langle\frac{1}{r}\rangle = \int_0^\infty \frac{1}{r}R_{n\ell}^2 r^2 dr = \frac{1}{n^2}(\frac{Z}{a})$$

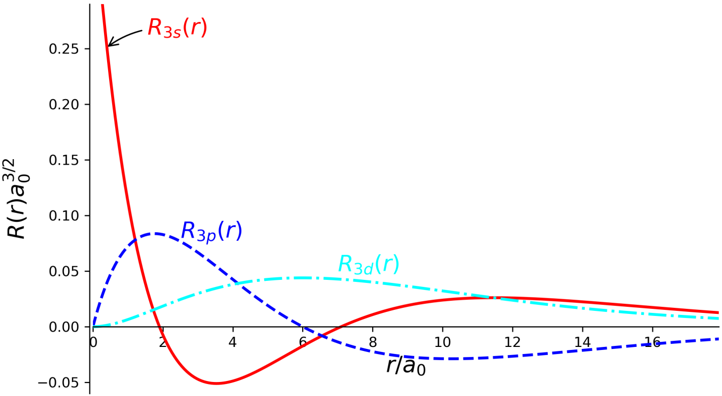
$$\langle\frac{1}{r^3}\rangle = \frac{1}{\ell(\ell+1/2)(\ell+1)}(\frac{Z}{na})^3$$

R_{1s} & R_{2s} & R_{2p}



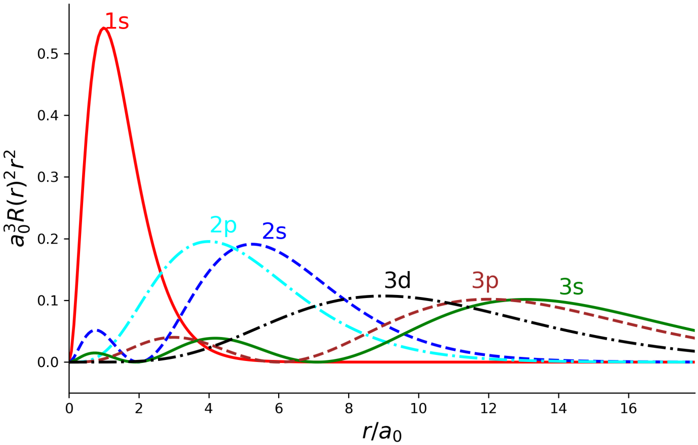
Electron in the Nucleus?!

R_{3s} & R_{3p} & R_{3d}



$R_{3s}(r)$
$R_{3p}(r)$
$R_{3d}(r)$
$R(r)a_0^{3/2}$
r/a_0
0.25
0.20
0.15
0.10
0.05
0.00
−0.05
0
2
4
6
8
10
12
14
16

Radial Distribution Function $R_{n\ell}^2 r^2$



Real Hydrogenlike Functions

$$\Psi_{n,\ell,m} = R_{n\ell}(r) S_{\ell m}(\theta) \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

combinations of $\Psi_{n,\ell,m}$ and $\Psi_{n,\ell,-m}$:

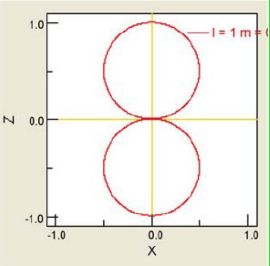
$$\Psi_{n,\ell,|m|} = R_{n\ell}(r) S_{\ell,|m|}(\theta) \frac{1}{\sqrt{2\pi}} \left\{ \begin{array}{l} \cos |m|\phi \\ \sin |m|\phi \end{array} \right.$$

$$\begin{aligned}
\Psi_{2p_z} &= \Psi_{2p_0} = \frac{1}{\sqrt{\pi}} (\frac{Z}{2a})^{5/2} e^{-Zr/2a} z \\
\Psi_{2p_x} &= \frac{1}{\sqrt{2}} (\Psi_{2p_1} + \Psi_{2p_{-1}}) = \frac{1}{\sqrt{\pi}} (\frac{Z}{2a})^{5/2} e^{-Zr/2a} x \\
\Psi_{2p_y} &= \frac{1}{i\sqrt{2}} (\Psi_{2p_1} - \Psi_{2p_{-1}}) = \frac{1}{\sqrt{\pi}} (\frac{Z}{2a})^{5/2} e^{-Zr/2a} y \\
\Psi_{3d_{xy}} &= \frac{1}{i\sqrt{2}} (\Psi_{3d_2} - \Psi_{3d_{-2}}) = \frac{2}{81\sqrt{2\pi}} (\frac{Z}{a})^{7/2} e^{-Zr/3a} xy
\end{aligned}$$

Graphs of Real Hydrogenlike Orbitals

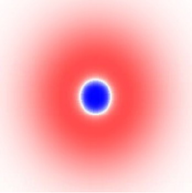
- Angular wave function, $|Y_{\ell m}(\theta, \phi)|$

p_z

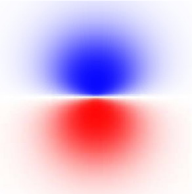


- Probability density, $|\Psi|^2$, $|\Psi|$ ($@y = 0$)

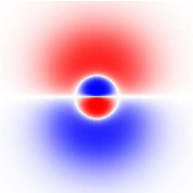
2s



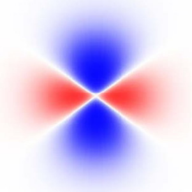
2pz



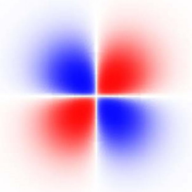
3pz



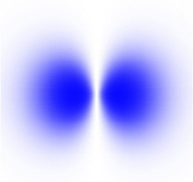
$3d_{z^2}$



$3d_{xz}$



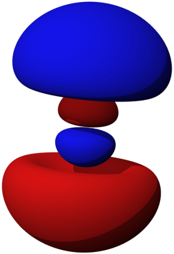
$3d_{x^2-y^2}$



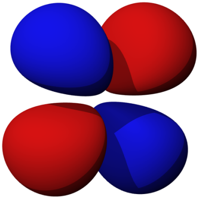
A Java viewer from: http://www.falstad.com/qmatom/

Graphs of Real Hydrogenlike Orbitals

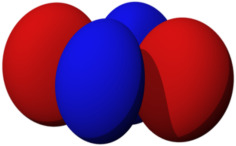
$3p_z \quad (m = 0)$



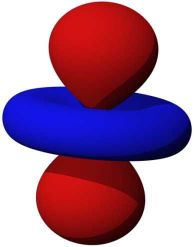
$3d_{xz} \quad (m = \pm 1)$



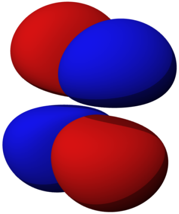
$3d_{xy} \quad (m = \pm 2)$



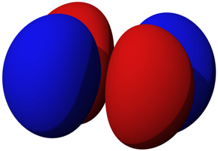
$3d_{z^2} \quad (m = 0)$



$3d_{yz} \quad (m = \pm 1)$

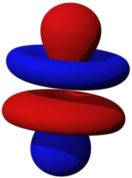


$3d_{x^2-y^2} \quad (m = \pm 2)$

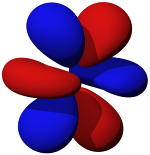


Graphs of Real Hydrogenlike Orbitals

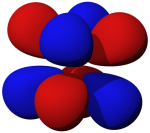
$4f_{z^3}$ $(m=0)$



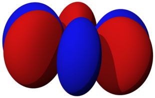
$4f_{xz^2}$ $(m=\pm1)$



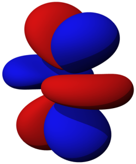
$4f_{xyz}$ $(m=\pm2)$



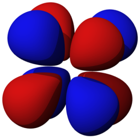
$4f_{x(x^2-3y^2)}$ $(m=\pm3)$



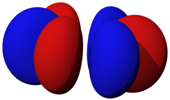
$4f_{yz^2}$ $(m=\pm1)$



$4f_{z(x^2-y^2)}$ $(m=\pm2)$

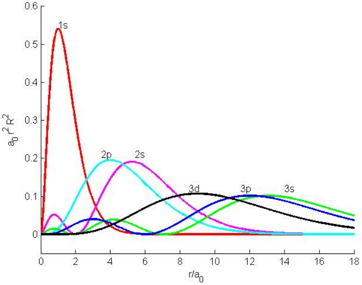


$4f_{y(3x^2-y^2)}$ $(m=\pm3)$



http://en.wikipedia.org/wiki/Atomic_orbital

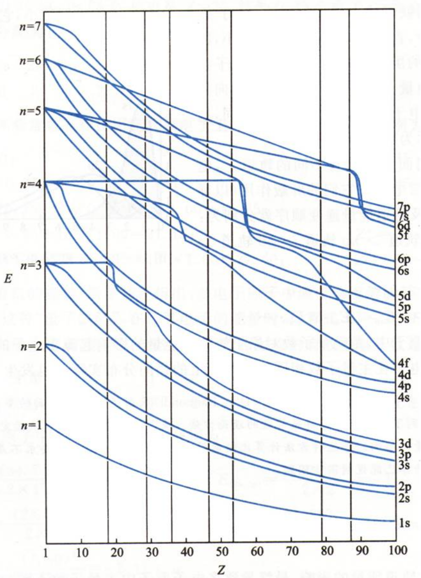
多电子原子的电子轨道能级



钻穿效应 Penetrating Effect

外层电子有穿过内层电子的布居；
$E(ns) < E(np) < E(nd) < E(nf)$；
能级交错。

原子轨道能级图



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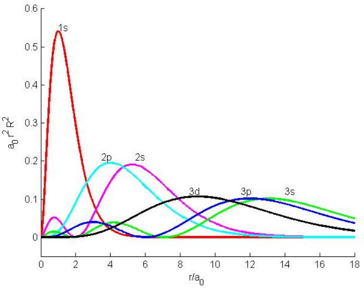

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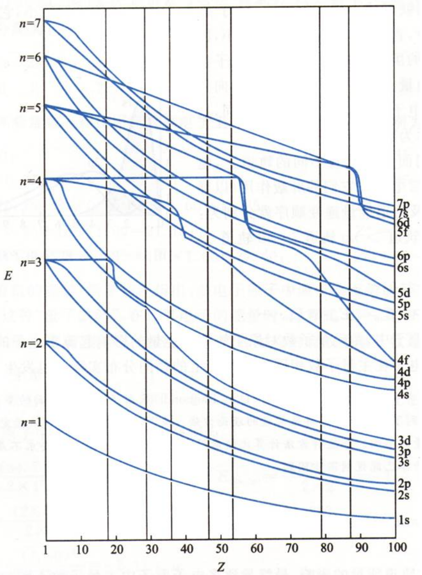
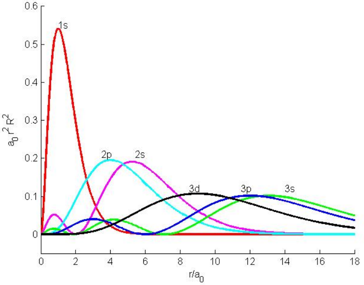


多电子原子的电子轨道能级



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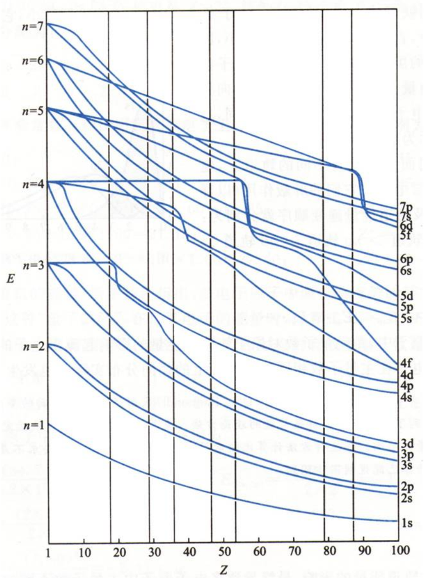

参考内容提纲

内容	参考书
氢原子的薛定谔方程	【Lv】§6.1 【杨】§17
多个独立粒子体系	【Lv】§6.2-6.3
单粒子三维中心力场	【Lv】§6.1 【曾】§6.1
类氢原子能级	【Lv】§6.5 【杨】§17
类氢原子波函数	【Lv】§6.6 【杨】§17