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## The one-electron atom

H ( $Z = 1$ ), He<sup>+</sup> ( $Z = 2$ ), Li<sup>2+</sup> ( $Z = 3$ ), ..., U<sup>91+</sup> ( $Z = 92$ ), ...

Electronic Hamilton operator (for point-like clamped nucleus)\*:

$$\widehat{H}_{\text{el}} = \widehat{T}_{\text{e}} + \widehat{V}_{\text{en}} = -\frac{\hbar^2}{2m_{\text{e}}}\nabla^2 - \frac{Z e^2}{\kappa_0 r} \quad (139)$$

Determination of stationary bound states, i.e. solutions  $\langle \mathbf{r} | \psi \rangle = \psi(\mathbf{r})$  with  $E < 0$ , to the time-independent Schrödinger equation (with  $\widehat{H}_{\text{el}}$  from above):

$$(\widehat{H}_{\text{el}} - E) \psi(\mathbf{r}) = \left( -\frac{\hbar^2}{2m_{\text{e}}}\nabla^2 - \frac{Z e^2}{\kappa_0 r} - E \right) \psi(\mathbf{r}) = 0 \quad (140)$$

Firstly, we remove the fundamental constants by switching to 'atomic units'. This reduces the mathematical work to pure numbers, and eliminates quantities which have experimental uncertainties.

\*The finite mass of the nucleus can be taken into account by switching from the electron mass  $m_{\text{e}}$  to a reduced mass  $\mu$ , where  $\mu^{-1} = m_{\text{e}}^{-1} + m_{\text{N}}^{-1}$  and  $m_{\text{N}}$  is the nuclear mass.

## Atomic units<sup>a</sup>

Physical quantity	Symbol (name)	Value in SI units <sup>b</sup>		
mass	$m_e$	9.1093826(16)	$\times 10^{-31}$	kg
charge	$e$	1.60217653(14)	$\times 10^{-19}$	C
angular momentum, action	$\hbar$	1.05457168(18)	$\times 10^{-34}$	J s
el. permittivity $4\pi\epsilon_0$	$\kappa_0$	1.112650056...	$\times 10^{-10}$	F m <sup>-1</sup>
length $\kappa_0\hbar^2/(m_e e^2) = \hbar/(\alpha m_e c)$	$a_0$ (bohr)	5.291772	$\times 10^{-11}$	m
time $\hbar/E_h = \hbar/(\alpha^2 m_e c^2)$		2.418884	$\times 10^{-17}$	s
velocity $a_0 E_h/\hbar = \alpha c$		2.187691	$\times 10^6$	m s <sup>-1</sup>
linear momentum $\hbar/a_0 = \alpha m_e c$		1.992852	$\times 10^{-24}$	kg m s <sup>-1</sup>
force $E_h/a_0$		8.238723	$\times 10^{-8}$	N
energy $e^2/(\kappa_0 a_0) = \alpha^2 m_e c^2$	$E_h$ (hartree)	4.359744	$\times 10^{-18}$	J
power $E_h^2/\hbar$		1.802378	$\times 10^{-1}$	W
charge density $e/a_0^3$		1.081202	$\times 10^{12}$	C m <sup>-3</sup>
el. current $eE_h/\hbar$		6.623618	$\times 10^{-3}$	A
el. potential $E_h/e$		2.721138	$\times 10^1$	V
el. capacitance $\kappa_0 a_0$		5.887891	$\times 10^{-21}$	F
el. resistance $\hbar/e^2$		4.108236	$\times 10^3$	$\Omega$
el. field strength ( $\mathbf{E}$ ) $E_h/(ea_0)$		5.142206	$\times 10^{11}$	V m <sup>-1</sup>
el. displacement ( $\mathbf{D}$ ) $e/a_0^2$		5.721476	$\times 10^1$	C m <sup>-2</sup>
el. dipole moment $ea_0$		8.478353	$\times 10^{-30}$	C m
el. quadrupole moment $ea_0^2$		4.486551	$\times 10^{-40}$	C m <sup>2</sup>
el. polarizability $(ea_0)^2/E_h$		1.648777	$\times 10^{-41}$	C <sup>2</sup> m <sup>2</sup> J <sup>-1</sup>
magn. flux $\hbar/e$		6.582119	$\times 10^{-16}$	Wb
magn. flux density ( $\mathbf{B}$ ) $\hbar/(ea_0^2)$		2.350517	$\times 10^5$	T
magnetizing force ( $\mathbf{H}$ ) $eE_h/(a_0\hbar)$		1.251682	$\times 10^8$	A m <sup>-1</sup>
magn. dipole moment $e\hbar/m_e = 2\mu_B$		1.854802	$\times 10^{-23}$	J T <sup>-1</sup>

<sup>a</sup>Based on CODATA recommended values 2002 (<http://physics.nist.gov/constants/>).

<sup>b</sup>The standard deviation uncertainty in the least significant digits is given in parentheses.

Now the Schrödinger equation reads

$$\left(\widehat{H}_{el} - E\right) \psi(\mathbf{r}) = \left(-\frac{1}{2}\nabla^2 - \frac{Z}{r} - E\right) \psi(\mathbf{r}) = 0 \quad (141)$$

which is transformed from cartesian coordinates  $(x, y, z)$  to spherical coordinates  $(r, \theta, \phi)$ , with  $0 \leq r < \infty$ ,  $0 \leq \theta \leq \pi$ , and  $0 \leq \phi \leq 2\pi$ .

Laplace operator  $\Delta$  and squared angular momentum operator  $\widehat{l}^2$  (in atomic units) in spherical coordinates:

$$\Delta = \nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{\widehat{l}^2}{r^2} = \frac{1}{r} \frac{\partial^2}{\partial r^2} r - \frac{\widehat{l}^2}{r^2} \quad (142)$$

$$\widehat{l}^2 = - \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} \quad (143)$$

Separation ansatz for the state function:

$$\psi(\mathbf{r}) = \psi(r, \theta, \phi) = R(r) Y(\theta, \phi) \quad (144)$$

(this is always possible for 'central fields', i.e.  $V = V(r)$ ).

The angular part is found to be a spherical harmonic,  $Y(\theta, \phi) = Y_{lm}(\theta, \phi)$ , which is an 'angular momentum eigenfunction', i.e. a simultaneous eigenfunction of  $\hat{l}^2$  and  $\hat{l}_z$  (in atomic units):

$$\hat{l}^2 Y_{lm}(\theta, \phi) = l(l+1) Y_{lm}(\theta, \phi) \quad (145)$$

$$\hat{l}_z Y_{lm}(\theta, \phi) = m Y_{lm}(\theta, \phi) \quad (146)$$

Orbital angular momentum quantum number  $l$ :  $l = 0, 1, 2, 3, \dots$ ,  
Magnetic quantum number  $m$ :  $-l \leq m \leq l$ .

Explicit form for the spherical harmonics (with Condon-Shortley<sup>†</sup> phase convention),  $-l \leq m \leq l$ :

$$Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta) \Phi_m(\phi) = (-1)^m N_{lm} P_l^m(\cos \theta) e^{im\phi} \quad (147)$$

$$N_{lm} = \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}}, \quad Y_{l,-m}(\theta, \phi) = (-1)^m Y_{lm}^*(\theta, \phi)$$

$$\int_{\Omega} Y_{lm}^*(\theta, \phi) Y_{l'm'}(\theta, \phi) d\Omega = \delta_{ll'} \delta_{mm'}$$

<sup>†</sup> E. U. Condon (1902-1974), G. H. Shortley (\*1910)

Notation for single-particle eigenfunctions of angular momentum:

$$\hat{l}^2 |\psi_{\alpha lm}\rangle = l(l+1) \hbar^2 |\psi_{\alpha lm}\rangle$$

$$\hat{l}_z |\psi_{\alpha lm}\rangle = m \hbar |\psi_{\alpha lm}\rangle$$

$l$	0	1	2	3	4	5	6	7	8	9	10	...
	s	p	d	f	g	h	i	k	l	m	n	...

Notation for many-particle eigenfunctions of total angular momentum:

$$\hat{L}^2 |\Psi_{\alpha LM}\rangle = L(L+1) \hbar^2 |\Psi_{\alpha LM}\rangle$$

$$\hat{L}_z |\Psi_{\alpha LM}\rangle = M \hbar |\Psi_{\alpha LM}\rangle$$

$$\hat{L}_z = \sum_{i=1}^n \hat{l}_{z,i}, \quad \hat{L} = \sum_{i=1}^n \hat{l}_i, \quad \hat{L}^2 = \hat{L} \cdot \hat{L}$$

$L$	0	1	2	3	4	5	6	7	8	9	10	...
	S	P	D	F	G	H	I	K	L	M	N	...

The associated Legendre<sup>‡</sup> functions  $P_l^m(\cos \theta)$  are related to the Legendre polynomials  $P_l(x) = P_l^0(x)$  ( $x = \cos \theta$ ). The following relations hold (for  $-l \leq m \leq l$ , where applicable):

$$P_l^m(x) = \frac{1}{2^l l!} (1-x^2)^{m/2} \frac{d^{l+m}}{dx^{l+m}} (x^2-1)^l \quad (148)$$

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2-1)^l = {}_2F_1(-l, l+1; 1; (1-x)/2) \quad (149)$$

$$P_l^{-m}(x) = (-1)^m \frac{(l-m)!}{(l+m)!} P_l^m(x) \quad (150)$$

$$P_{l+1}^m(x) = \frac{2l+1}{l-m+1} x P_l^m(x) - \frac{l+m}{l-m+1} P_{l-1}^m(x) \quad (151)$$

$$P_l^{m+1}(x) = \frac{2m}{\sqrt{1-x^2}} x P_l^m(x) - (l+m)(l-m+1) P_l^{m-1}(x) \quad (152)$$

<sup>‡</sup> A.-M. Legendre (1752-1833)

### The first Legendre polynomials

$l$	$P_l(x)$
0	1
1	$x$
2	$\frac{1}{2} (3x^2 - 1)$
3	$\frac{1}{2} (5x^3 - 3x)$
4	$\frac{1}{8} (35x^4 - 30x^2 + 3)$
5	$\frac{1}{8} (63x^5 - 70x^3 + 15x)$

The first associated Legendre functions

$l$	$m$	$P_l^m(\cos\theta)$	$l$	$m$	$P_l^m(\cos\theta)$
0	0	1	3	0	$\frac{1}{2}(5\cos^3\theta - 3\cos\theta)$
1	0	$\cos\theta$	3	+1	$\frac{3}{2}\sin\theta(5\cos^2\theta - 1)$
1	+1	$\sin\theta$	3	-1	$-\frac{1}{8}\sin\theta(5\cos^2\theta - 1)$
1	-1	$-\frac{1}{2}\sin\theta$	3	+2	$15\sin^2\theta\cos\theta$
2	0	$\frac{1}{2}(3\cos^2\theta - 1)$	3	-2	$\frac{1}{8}\sin^2\theta\cos\theta$
2	+1	$3\sin\theta\cos\theta$	3	+3	$15\sin^3\theta$
2	-1	$-\frac{1}{2}\sin\theta\cos\theta$	3	-3	$-\frac{1}{48}\sin^3\theta$
2	+2	$3\sin^2\theta$			
2	-2	$\frac{1}{8}\sin^2\theta$			

The first spherical harmonics  
(Condon-Shortley phase convention)

$l$	$m$	$Y_{lm}(\theta, \phi)$	$l$	$m$	$Y_{lm}(\theta, \phi)$
0	0	$\sqrt{\frac{1}{4\pi}}$	3	+3	$-15\sqrt{\frac{7}{2880\pi}}\sin^3\theta e^{3i\phi}$
1	+1	$-\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi}$	3	+2	$15\sqrt{\frac{7}{480\pi}}\sin^2\theta\cos\theta e^{2i\phi}$
1	0	$\sqrt{\frac{3}{4\pi}}\cos\theta$	3	+1	$-\frac{3}{2}\sqrt{\frac{7}{48\pi}}\sin\theta(5\cos^2\theta - 1)e^{i\phi}$
1	-1	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi}$	3	0	$\frac{1}{2}\sqrt{\frac{7}{4\pi}}(5\cos^3\theta - 3\cos\theta)$
2	+2	$3\sqrt{\frac{5}{96\pi}}\sin^2\theta e^{2i\phi}$	3	-1	$\frac{3}{2}\sqrt{\frac{7}{48\pi}}\sin\theta(5\cos^2\theta - 1)e^{-i\phi}$
2	+1	$-3\sqrt{\frac{5}{24\pi}}\sin\theta\cos\theta e^{i\phi}$	3	-2	$15\sqrt{\frac{7}{480\pi}}\sin^2\theta\cos\theta e^{-2i\phi}$
2	0	$\frac{1}{2}\sqrt{\frac{5}{4\pi}}(3\cos^2\theta - 1)$	3	-3	$15\sqrt{\frac{7}{2880\pi}}\sin^3\theta e^{-3i\phi}$
2	-1	$3\sqrt{\frac{5}{24\pi}}\sin\theta\cos\theta e^{-i\phi}$			
2	-2	$3\sqrt{\frac{5}{96\pi}}\sin^2\theta e^{-2i\phi}$			

Two-point boundary value problem for  $P(r) = r R(r)$  (as resulting from the separation ansatz):

$$\left( \frac{d^2}{dr^2} + 2 [ E - V_l(r) ] \right) P(r) = 0 \quad (153)$$

$$V_l(r) = \frac{l(l+1)}{2r^2} - \frac{Z}{r}, \quad P(0) = 0, \quad \lim_{r \rightarrow \infty} P(r) = 0$$

Physically acceptable (i.e. normalizable) solutions exist only for a discrete set of energies: **Quantization** due to the **boundary conditions**.

Radial functions (eigenfunctions):

$$P_{nl}(r) = r R_{nl}(r) = N_{nl} x^{l+1} L_{n_r}^{(2l+1)}(x) e^{-x/2} \quad (154)$$

$$x = \frac{2Z}{n} r, \quad N_{nl} = \frac{1}{n} \sqrt{Z \frac{n_r!}{(n+l)!}}, \quad n_r = n - l - 1 \geq 0$$

$$\int_0^\infty R_{nl}(r) R_{n'l}(r) r^2 dr = \int_0^\infty P_{nl}(r) P_{n'l}(r) dr = \delta_{nn'}$$

Energy eigenvalues (in atomic units):

$$E_n = E_{nlm} = -\frac{1}{2} \frac{Z^2}{n^2} \quad (155)$$

These are **degenerate** for  $n > 1$  (further details below).  
Principal quantum number  $n$ :  $n = 1, 2, 3, \dots$

This result for  $E_n$  is also an important hint for the understanding of the stability of matter:  $E_n > -\infty$ , i.e. the electron does not collapse into the nucleus, despite the singular attractive potential, due to a **balance between kinetic and potential energy**.

Generalized Laguerre<sup>§</sup> polynomials:

$$L_k^{(\alpha)}(x) = \frac{(\alpha+1)_k}{k!} {}_1F_1(-k; \alpha+1; x) \quad (156)$$

$$L_k^{(\alpha)}(x) = \frac{2k + \alpha - 1 - x}{k} L_{k-1}^{(\alpha)}(x) - \frac{k + \alpha - 1}{k} L_{k-2}^{(\alpha)}(x) \quad (k \geq 2) \quad (157)$$

<sup>§</sup> E. N. Laguerre (1834-1886)

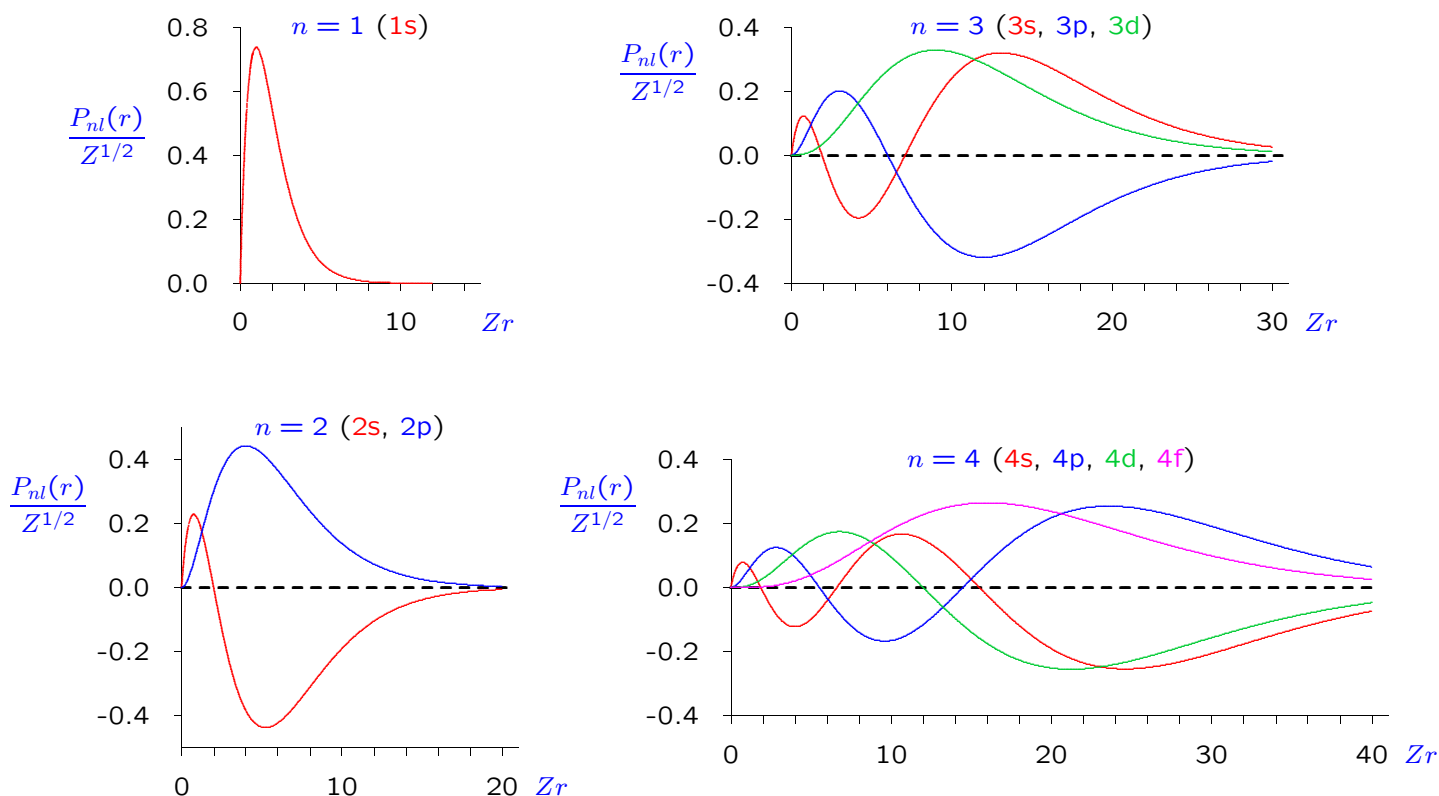
## The first generalized Laguerre polynomials

$k$	$L_k^{(\alpha)}(x)$
0	1
1	$(\alpha + 1) - x$
2	$\frac{1}{2} \left[ (\alpha + 1)(\alpha + 2) - 2(\alpha + 2)x + x^2 \right]$
3	$\frac{1}{6} \left[ (\alpha + 1)(\alpha + 2)(\alpha + 3) - 3(\alpha + 2)(\alpha + 3)x + 3(\alpha + 3)x^2 - x^3 \right]$
4	$\frac{1}{24} \left[ (\alpha + 1)(\alpha + 2)(\alpha + 3)(\alpha + 4) - 4(\alpha + 2)(\alpha + 3)(\alpha + 4)x + 6(\alpha + 3)(\alpha + 4)x^2 - 4(\alpha + 4)x^3 + x^4 \right]$
5	$\frac{1}{120} \left[ (\alpha + 1)(\alpha + 2)(\alpha + 3)(\alpha + 4)(\alpha + 5) - 5(\alpha + 2)(\alpha + 3)(\alpha + 4)(\alpha + 5)x + 10(\alpha + 3)(\alpha + 4)(\alpha + 5)x^2 - 10(\alpha + 4)(\alpha + 5)x^3 + 5(\alpha + 5)x^4 - x^5 \right]$

### The first radial functions of one-electron atoms

	$n$	$l$	$n_r$	$P_{nl}(r)$ ( $x = 2Zr/n$ )
1s	1	0	0	$\sqrt{Z} x e^{-x/2}$
2s	2	0	1	$\frac{1}{2} \sqrt{\frac{Z}{2}} x (2 - x) e^{-x/2}$
2p	2	1	0	$\frac{1}{2} \sqrt{\frac{Z}{6}} x^2 e^{-x/2}$
3s	3	0	2	$\frac{1}{3} \sqrt{\frac{Z}{3}} x (3 - 3x + x^2/2) e^{-x/2}$
3p	3	1	1	$\frac{1}{3} \sqrt{\frac{Z}{24}} x^2 (4 - x) e^{-x/2}$
3d	3	2	0	$\frac{1}{3} \sqrt{\frac{Z}{120}} x^3 e^{-x/2}$
4s	4	0	3	$\frac{1}{4} \sqrt{\frac{Z}{4}} x (4 - 6x + 2x^2 - x^3/6) e^{-x/2}$
4p	4	1	2	$\frac{1}{4} \sqrt{\frac{Z}{60}} x^2 (10 - 5x + x^2/2) e^{-x/2}$
4d	4	2	1	$\frac{1}{4} \sqrt{\frac{Z}{720}} x^3 (6 - x) e^{-x/2}$
4f	4	3	0	$\frac{1}{4} \sqrt{\frac{Z}{5040}} x^4 e^{-x/2}$

Radial functions  $P_{nl}(r)$  of the one-electron atom (for  $n = 1, 2, 3, 4$ )



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Eigenfunctions and energy eigenvalues (in atomic units) of the one-electron atom:

$$\psi_{nlm}(\mathbf{r}) = \frac{1}{r} P_{nl}(r) Y_{lm}(\theta, \phi), \quad E_{nlm} = E_n = -\frac{1}{2} \frac{Z^2}{n^2} \quad (158)$$

$$n = 1, 2, 3, 4, \dots, \quad l = 0, 1, \dots, n-1, \quad m = -l, -l+1, \dots, l$$

$$\langle nlm | n'l'm' \rangle = \int \psi_{nlm}(\mathbf{r}) \psi_{n'l'm'}(\mathbf{r}) d\mathbf{r} = \delta_{nn'} \delta_{ll'} \delta_{mm'}$$

Ground state and corresponding energy:

$$\psi_{100}(\mathbf{r}) = \sqrt{\frac{Z^3}{\pi}} e^{-Zr} = \frac{1}{r} \sqrt{Z} 2Zr e^{-Zr} \frac{1}{\sqrt{4\pi}}, \quad E_1 = -\frac{Z^2}{2} \quad (159)$$

For isovalue plots — i.e. representations of all points  $\mathbf{r}$  with  $\psi_{nlm}(\mathbf{r}) = |c|$  for chosen  $c \in \mathbb{R}$  — of the eigenfunctions of the one-electron atom, see J. Brickmann, M. Klöffler, H.-U. Raab, *Chemie in unserer Zeit* **12** (1978) 23-26.

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Degree of degeneracy<sup>¶</sup>:

$$m \text{ degeneracy: } g_l = \sum_{m=-l}^l 1 = 2l + 1 \quad (160)$$

$$l \text{ degeneracy (without spin): } g_n = \sum_{l=0}^{n-1} g_l = n^2 \quad (161)$$

$$l \text{ degeneracy (spin included): } g_n^s = 2 g_n = 2 n^2 \quad (162)$$

The value  $g_n^s$  essentially determines the length of the rows ('periods') in the table of chemical elements (2, 8, 18, 32), whereas the value  $2 g_l = 2(2l + 1)$  determines the block structure of the 'periodic' table (s-, p-, d-, and f-block for  $l = 0, 1, 2, 3$ , respectively).

<sup>¶</sup> The degeneracy with respect to  $l$ , eq. (161), is a special property of the one-electron atom (with point-like nucleus), and is not present in many-electron atoms. For example, the 2s and 2p states of a one-electron atom are degenerate, i.e. they have the same energy, but the 'orbital energies' for the 2s and 2p orbitals in any state of a many-electron atom are always different.

## The 'periodic' table of the chemical elements (2004)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 ✓	112 (✓)	113	114 (✓)	115	116 (✓)	117	118 (?)

	*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
	**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

## The variation principle at work (I)

The ground state  $1s^1 \ ^2S$  of the one-electron atom

Definition of the system under consideration:

$$\hat{H} = \hat{T} + \hat{V}, \quad \hat{T} = -\frac{1}{2}\Delta, \quad \hat{V} = V_{\text{nuc}}(r) = -\frac{Z}{r}$$

A set of trial functions<sup>||</sup>:

1. Slater function ( $\zeta > 0$ ):

$$\psi_S = N_S \exp(-\zeta r)$$

3. Lorentz function ( $a > 0$ ):

$$\psi_L = N_L [1 + (ar)^2]^{-1}$$

2. Gauß function ( $\alpha > 0$ ):

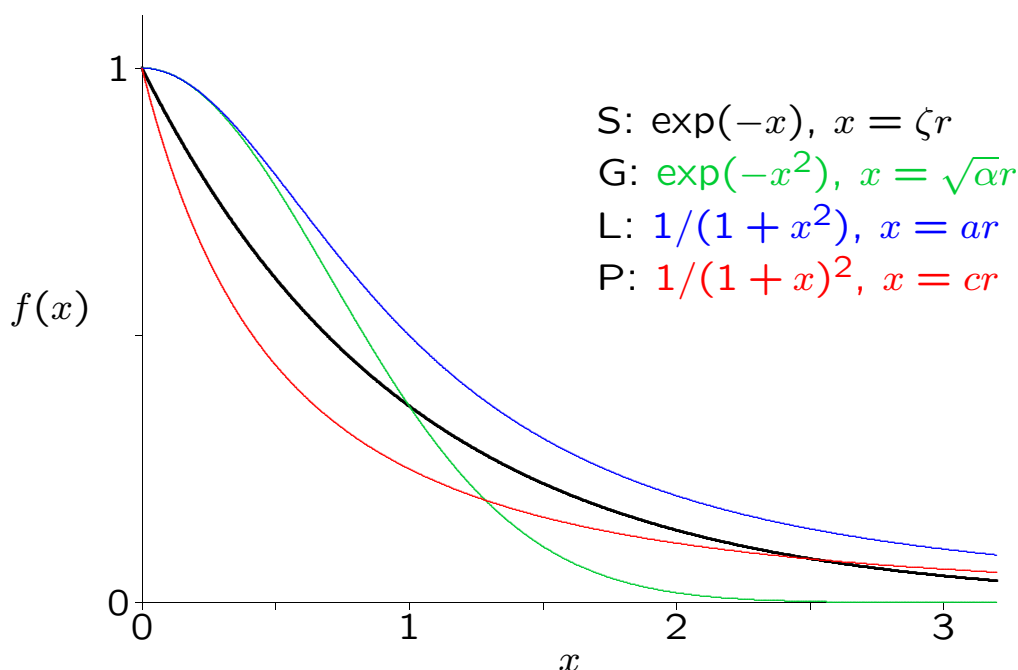
$$\psi_G = N_G \exp(-\alpha r^2)$$

4. Preuß function ( $c > 0$ ):

$$\psi_P = N_P [1 + cr]^{-2}$$

<sup>||</sup>Refs.: C. Zener, Phys. Rev. **36** (1930) 51, J. C. Slater, Phys. Rev. **36** (1930) 57 (Slater function) — S. F. Boys, Proc. R. Soc. London A **200** (1950) 542, H. Preuß, Z. Naturforsch. A **11** (1956) 823 (Gauß function) — H. Preuß, Z. Naturforsch. A **13** (1958) 439 (Preuß function).

Trial functions (unnormalized)  
for the ground state of the one-electron atom



Estimate for the ground state energy:

$$\langle E \rangle = \langle H \rangle = \langle \psi | \widehat{H} | \psi \rangle = \int \psi(\mathbf{r}) \widehat{H} \psi(\mathbf{r}) d\mathbf{r} = \langle T \rangle + \langle V \rangle$$

$$\langle T \rangle = -\frac{1}{2} \langle \psi | \Delta | \psi \rangle = +\frac{1}{2} \langle \nabla \psi | \nabla \psi \rangle, \quad \langle V \rangle = -Z \langle r^{-1} \rangle$$

Mathematical preliminaries:

- The beta function:

$$B(a, b) = \frac{\Gamma(a) \Gamma(b)}{\Gamma(a+b)} = B(b, a)$$

$$B(a, b) = \int_0^1 t^{a-1} (1-t)^{b-1} dt = \int_0^\infty \frac{t^{a-1}}{(1+t)^{a+b}} dt \quad (a > 0, b > 0)$$

- Useful integral formulas:

$$\int_0^\infty x^{s-1} \exp(-p x^n) dx = \frac{1}{n} \frac{\Gamma(s/n)}{p^{s/n}} \quad (p > 0, s/n > 0)$$

$$\int_0^\infty \frac{x^{s-1}}{(1+x^n)^p} dx = \frac{1}{n} B(p - s/n, s/n) \quad (s/n > 0, np - s > 0)$$

1. The Slater function  $\psi_S = N_S \exp(-\zeta r)$ ,  $\zeta_{\text{opt}} = ?$ :

$$\langle r^k \rangle = N_S^2 4\pi \int_0^\infty dr r^{k+2} e^{-2\zeta r} = N_S^2 4\pi \frac{\Gamma(k+3)}{(2\zeta)^{k+3}} \quad (k > -3)$$

$$\langle 1 \rangle = \langle r^0 \rangle = N_S^2 \frac{\pi}{\zeta^3} \equiv 1 \quad \Rightarrow \quad N_S = \sqrt{\zeta^3/\pi}$$

$$\langle r^k \rangle = \frac{\Gamma(k+3)}{2^{k+1}} \frac{1}{\zeta^k}$$

$$\begin{aligned} \langle T \rangle &= +\frac{1}{2} N_S^2 \frac{4\pi}{\zeta} \int_0^\infty dx \left( \frac{d}{dx} x e^{-x} \right)^2 \\ &= \frac{1}{2} N_S^2 \frac{4\pi}{\zeta} \int_0^\infty dx (1-x)^2 e^{-2x} = \frac{1}{2} \zeta^2 \end{aligned}$$

$$\langle V \rangle = -Z \zeta$$

$$\langle E \rangle = \frac{1}{2} \zeta^2 - Z \zeta \quad \Rightarrow \quad \frac{d\langle E \rangle}{d\zeta} = \zeta - Z = 0 \quad \Rightarrow \quad \zeta_{\text{opt}} = Z$$

$$\frac{\langle E \rangle}{Z^2} = x \left( \frac{1}{2} x - 1 \right) \quad (x = \zeta/Z) \quad \Rightarrow \quad E_{\text{min}} = -\frac{1}{2} Z^2$$

2. The Gauß function  $\psi_G = N_G \exp(-\alpha r^2)$ ,  $\alpha_{\text{opt}} = ?$ :

$$\langle r^k \rangle = N_G^2 4\pi \int_0^\infty dr r^{k+2} e^{-2\alpha r^2} = N_G^2 4\pi \frac{1}{2} \frac{\Gamma(\frac{k+3}{2})}{(2\alpha)^{\frac{k+3}{2}}} \quad (k > -3)$$

$$\langle 1 \rangle = \langle r^0 \rangle = N_G^2 \left(\frac{\pi}{2\alpha}\right)^{3/2} \equiv 1 \quad \Rightarrow \quad N_G = \left(\frac{2\alpha}{\pi}\right)^{3/4}$$

$$\langle r^k \rangle = \frac{2}{\sqrt{\pi}} \frac{\Gamma(\frac{k+3}{2})}{(2\alpha)^{k/2}}$$

$$\begin{aligned} \langle T \rangle &= + \frac{1}{2} N_G^2 \frac{4\pi}{\sqrt{\alpha}} \int_0^\infty dx \left(\frac{d}{dx} x e^{-x^2}\right)^2 \\ &= \frac{1}{2} N_G^2 \frac{4\pi}{\sqrt{\alpha}} \int_0^\infty dx (1 - 2x^2)^2 e^{-2x^2} = \frac{3}{2} \alpha \end{aligned}$$

$$\langle V \rangle = -2Z \sqrt{2\alpha/\pi}$$

$$\langle E \rangle = \frac{3}{2} \alpha - 2Z \sqrt{\frac{2\alpha}{\pi}} \Rightarrow \frac{d\langle E \rangle}{d\alpha} = \frac{3}{2} - Z \sqrt{\frac{2}{\pi\alpha}} = 0 \Rightarrow \alpha_{\text{opt}} = \frac{8Z^2}{9\pi}$$

$$\frac{\langle E \rangle}{Z^2} = x \left(\frac{3}{2} x - 2\sqrt{\frac{2}{\pi}}\right) \quad (x = \sqrt{\alpha}/Z) \quad \Rightarrow \quad E_{\text{min}} = -\frac{4}{3\pi} Z^2$$

3. The Lorentz function  $\psi_L = N_L [1 + (ar)^2]^{-1}$ ,  $a_{\text{opt}} = ?$ :

$$\langle r^k \rangle = N_L^2 4\pi \int_0^\infty \frac{r^{k+2} dr}{(1 + (ar)^2)^2} = N_L^2 \frac{4\pi}{a^{k+3}} \frac{1}{2} B\left(\frac{1-k}{2}, \frac{k+3}{2}\right)$$

$$\langle 1 \rangle = \langle r^0 \rangle = N_L^2 \frac{\pi^2}{a^3} \equiv 1 \quad \Rightarrow \quad N_L = \sqrt{a^3/\pi}$$

$$\langle r^k \rangle = \frac{2}{\pi} \frac{1}{a^k} B\left(\frac{1-k}{2}, \frac{k+3}{2}\right) \quad (-3 < k < 1)$$

$$\begin{aligned} \langle T \rangle &= + \frac{1}{2} N_L^2 \frac{4\pi}{a} \int_0^\infty dx \left(\frac{d}{dx} \frac{x}{1+x^2}\right)^2 \\ &= \frac{1}{2} N_L^2 \frac{4\pi}{a} \int_0^\infty dx \frac{(1-x^2)^2}{(1+x^2)^4} = \frac{1}{4} a^2 \end{aligned}$$

$$\langle V \rangle = -2Z a/\pi$$

$$\langle E \rangle = \frac{1}{4} a^2 - 2Z \frac{a}{\pi} \Rightarrow \frac{d\langle E \rangle}{da} = \frac{1}{2} a - Z \frac{2}{\pi} = 0 \Rightarrow a_{\text{opt}} = \frac{4Z}{\pi}$$

$$\frac{\langle E \rangle}{Z^2} = x \left(\frac{1}{4} x - \frac{2}{\pi}\right) \quad (x = a/Z) \quad \Rightarrow \quad E_{\text{min}} = -\frac{4}{\pi^2} Z^2$$

4. The Preuß function  $\psi_P = N_P [1 + cr]^{-2}$ ,  $c_{\text{opt}} = ?$ :

$$\langle r^k \rangle = N_P^2 4\pi \int_0^\infty \frac{r^{k+2} dr}{(1 + cr)^4} = N_P^2 \frac{4\pi}{c^{k+3}} B(1 - k, k + 3)$$

$$\langle 1 \rangle = \langle r^0 \rangle = N_P^2 \frac{4\pi}{3c^3} \equiv 1 \quad \Rightarrow \quad N_P = \sqrt{\frac{3c^3}{4\pi}}$$

$$\langle r^k \rangle = \frac{3}{c^k} B(1 - k, k + 3) \quad (-3 < k < 1)$$

$$\begin{aligned} \langle T \rangle &= + \frac{1}{2} N_P^2 \frac{4\pi}{c} \int_0^\infty dx \left( \frac{d}{dx} \frac{x}{(1+x)^2} \right)^2 \\ &= \frac{1}{2} N_P^2 \frac{4\pi}{c} \int_0^\infty dx \frac{(1-x)^2}{(1+x)^6} = \frac{1}{5} c^2 \end{aligned}$$

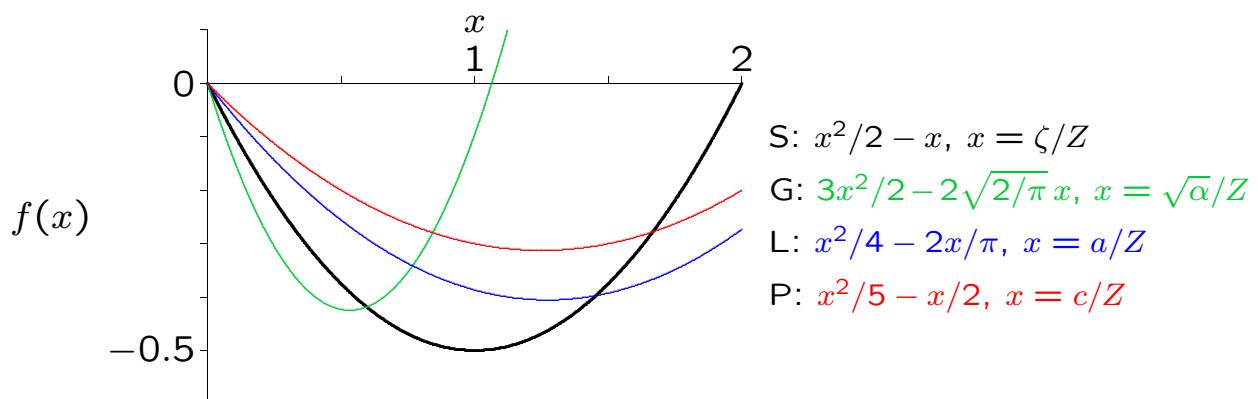
$$\langle V \rangle = -Zc/2$$

$$\langle E \rangle = \frac{1}{5} c^2 - Z \frac{c}{2} \Rightarrow \frac{d\langle E \rangle}{dc} = \frac{2}{5} c - \frac{Z}{2} = 0 \Rightarrow c_{\text{opt}} = \frac{5Z}{4}$$

$$\frac{\langle E \rangle}{Z^2} = x \left( \frac{1}{5} x - \frac{1}{2} \right) \quad (x = c/Z) \quad \Rightarrow \quad E_{\text{min}} = -\frac{5}{16} Z^2$$

Variation of the ground state energy  $\langle E \rangle$  of the one-electron atom with the trial function parameter

$$\frac{\langle E \rangle}{Z^2} = f(x) = a_2 x^2 + a_1 x$$



For optimal choice of the parameter  $x$  (i.e. at the minima), the quantum mechanical virial theorem,  $\langle V \rangle / \langle T \rangle = -2$ , is fulfilled, and thus  $\langle E \rangle = \langle V \rangle / 2 = -\langle T \rangle$  in all four cases.

## Perturbation theory

Time-independent Rayleigh-Schrödinger perturbation theory for non-degenerate states

Find a solution for the Schrödinger equation

$$\widehat{H}_\lambda \psi_\lambda = E_\lambda \psi_\lambda \quad \Leftrightarrow \quad (\widehat{H}_\lambda - E_\lambda) \psi_\lambda = 0 \quad (163)$$

with the Hamilton operator

$$\widehat{H}_\lambda = \widehat{H}^{(0)} + \sum_{k=1}^{\infty} \lambda^k \widehat{H}^{(k)}, \quad (164)$$

where  $\lambda$  is a (natural or artificial) perturbation parameter ( $|\lambda| < \lambda_{\max}$ ), and assume that the solutions of the unperturbed problem

$$\widehat{H}^{(0)} \psi^{(0)} = E^{(0)} \psi^{(0)} \quad (165)$$

are completely known (with all  $E^{(0)}$  non-degenerate). Then put

$$E_\lambda = E^{(0)} + \sum_{k=1}^{\infty} \varepsilon^{(k)} \lambda^k \quad \text{and} \quad \psi_\lambda = \psi^{(0)} + \sum_{l=1}^{\infty} \chi^{(l)} \lambda^l \quad (166)$$

into eq. (163):

$$\begin{aligned} 0 &= \left\{ \widehat{H}^{(0)} - E^{(0)} + \sum_{k=1}^{\infty} (\widehat{H}^{(k)} - \varepsilon^{(k)}) \lambda^k \right\} \left( \psi^{(0)} + \sum_{l=1}^{\infty} \chi^{(l)} \lambda^l \right) \\ &= (\widehat{H}^{(0)} - E^{(0)}) \psi^{(0)} + \sum_{m=1}^{\infty} \lambda^m \left\{ (\widehat{H}^{(0)} - E^{(0)}) \chi^{(m)} \right. \\ &\quad \left. + \sum_{k=1}^{m-1} (\widehat{H}^{(k)} - \varepsilon^{(k)}) \chi^{(m-k)} + (\widehat{H}^{(m)} - \varepsilon^{(m)}) \psi^{(0)} \right\} \end{aligned}$$

Thus we obtain from the coefficient of  $\lambda^m$ :

$$\begin{aligned} m = 0 : & \quad (\widehat{H}^{(0)} - E^{(0)}) \psi^{(0)} = 0 \\ m = 1 : & \quad (\widehat{H}^{(0)} - E^{(0)}) \chi^{(1)} + (\widehat{H}^{(1)} - E^{(1)}) \psi^{(0)} = 0 \\ m = 2 : & \quad (\widehat{H}^{(0)} - E^{(0)}) \chi^{(2)} + (\widehat{H}^{(1)} - E^{(1)}) \chi^{(1)} \\ & \quad + (\widehat{H}^{(2)} - E^{(2)}) \psi^{(0)} = 0 \\ & \quad \vdots \end{aligned}$$

The 'intermediate normalization' condition

$$\langle \psi^{(0)} | \psi_\lambda \rangle = 1 \quad \text{with} \quad \langle \psi^{(0)} | \psi^{(0)} \rangle = 1$$

implies orthogonality between  $\psi^{(0)}$  and all  $\chi^{(l)}$ :

$$\langle \psi^{(0)} | \chi^{(l)} \rangle = 0 \quad (\text{for } l = 1, 2, \dots)$$

Resulting expressions for  $\varepsilon^{(1)}$  and  $\varepsilon^{(2)}$ :

$$\varepsilon^{(1)} = \langle \psi^{(0)} | \widehat{H}^{(1)} | \psi^{(0)} \rangle \quad (167)$$

$$\varepsilon^{(2)} = \langle \psi^{(0)} | \widehat{H}^{(1)} | \chi^{(1)} \rangle + \langle \psi^{(0)} | \widehat{H}^{(2)} | \psi^{(0)} \rangle \quad (168)$$

The perturbation theory may be used advantageously

- to determine (non-variational) approximations to the solutions of eq. (163):

$$E_\lambda \approx E^{(n)} = E^{(0)} + \sum_{k=1}^n \varepsilon^{(k)} \lambda^k$$

$$\psi_\lambda \approx \psi^{(n)} = \psi^{(0)} + \sum_{l=1}^n \chi^{(l)} \lambda^l$$

- to obtain exact values for derivatives of the energy  $E$  or the state function  $\psi$  to various orders in  $\lambda$  at  $\lambda = 0$ , e.g.:

$$\left. \frac{\partial^n E}{\partial \lambda^n} \right|_{\lambda=0} = n! \varepsilon^{(n)}$$

The perturbation theory presented above can be extended to include the case of degenerate states.

## The two-electron atom

$H^-$  ( $Z = 1$ ), He ( $Z = 2$ ),  $Li^+$  ( $Z = 3$ ), ...,  $U^{90+}$  ( $Z = 92$ ), ...

Hamilton operator (in atomic units):

$$\hat{H}_{el} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} = \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} \quad (169)$$

General structure of state functions for two-electron systems\*\*:

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = f(\mathbf{r}_1, \mathbf{r}_2)\Theta(\sigma_1, \sigma_2)$$

Spin part  $\Theta = |SM_S\rangle$ : Singlet ( $S = 0$ , *para*-He) or triplet ( $S = 1$ , *ortho*-He)

$$\begin{aligned} |00\rangle &= (\alpha\beta - \beta\alpha)/\sqrt{2} \\ |11\rangle &= \alpha\alpha & |10\rangle &= (\alpha\beta + \beta\alpha)/\sqrt{2} & |1-1\rangle &= \beta\beta \end{aligned}$$

\*\* ... as long as the Hamilton operator does not act on the spin of the particles.

For the spatial part  $f(\mathbf{r}_1, \mathbf{r}_2)$  a suitable choice must be made. For S states we can simplify further to  $f(r_1, r_2, r_{12})$ , or equivalently  $f(s, t, u)$  with  $s = r_1 + r_2$ ,  $t = r_1 - r_2$ , and  $u = r_{12}$ .

Variational results for the helium ground state  $1s^2 \ ^1S^a$ .

$f(s, t, u)$	$-E_{opt}/a.u.$
$e^{-\zeta r_1} e^{-\zeta r_2} = e^{-\zeta s}$	2.8477
$\varphi(r_1)\varphi(r_2)$	2.8617 <sup>b</sup>
$e^{-\zeta r_1} e^{-\eta r_2} + e^{-\eta r_1} e^{-\zeta r_2}$	2.8757 <sup>c</sup>
$e^{-\zeta s + cu}$	2.8896
$e^{-\zeta s} (1 + cu)$	2.8911 <sup>d</sup>
$e^{-\zeta s + cu} \cosh(at)$	2.8994
$e^{-\zeta s} (c_0 + c_1 u + c_2 t^2 + c_3 s + c_4 s^2 + c_5 u^2)$	2.9032
exact	2.9037 <sup>e</sup>

<sup>a</sup> E. A. Hylleraas, *Z. Phys.* **54** (1929) 347

<sup>b</sup> C. Froese Fischer: *The Hartree-Fock method for atoms*. Wiley, New York, 1977

<sup>c</sup> C. Eckart, *Phys. Rev.* **36** (1930) 878

<sup>d</sup> W.-K. Li, *J. Chem. Educ.* **64** (1987) 128

<sup>e</sup> K. Frankowski, C. L. Pekeris, *Phys. Rev.* **146** (1966) 46

## The many-electron atom

A part of the knowledge of the state functions of the one-electron atom can be transferred to the **many-electron atom**, if the following assumptions are made<sup>††</sup>:

1. **Central field approximation:** The electrons in the many-electron atom are assumed to move in an effective central field  $V_{\text{eff},l}(r)$ , so that the orbitals can be written as  $\psi(\mathbf{r}) = R(r)Y(\theta, \phi)$ , with  $Y(\theta, \phi) = Y_{lm}(\theta, \phi)$ .
2. **Equivalence restriction:** The radial parts are assumed to be independent of the magnetic quantum number  $m$ :  $R(r) = R_{nl}(r)$ .

The resulting set of radial functions  $P_{nl}(r) = r R_{nl}(r)$  has to be determined for every state of the many-electron atom, e.g.

- He ground state (singlet):  $1s^2 \ ^1S \rightarrow P_{10}(r)$
- He excited states (singlet or triplet):  $1s^1 2s^1 \ ^1,^3S \rightarrow P_{10}(r), P_{20}(r)$
- Li ground state (doublet):  $1s^2 2s^1 \ ^2S \rightarrow P_{10}(r), P_{20}(r)$

<sup>††</sup> In addition to the approximation of the many-electron state function as a Slater determinant (an antisymmetrized product of spin orbitals), or a linear combination thereof.

### Electron configuration of neutral atoms in the ground state (designated as $^{2S+1}L_J$ )

1 H	$1s^1$	$^2S_{1/2}$	26 Fe	[Ar] $3d^6 4s^2$	$^5D_4$
2 He	$1s^2$	$^1S_0$	27 Co	[Ar] $3d^7 4s^2$	$^4F_{9/2}$
3 Li	[He] $2s^1$	$^2S_{1/2}$	28 Ni	[Ar] $3d^8 4s^2$	$^3F_4$
4 Be	[He] $2s^2$	$^1S_0$	29 Cu	[Ar] $3d^{10} 4s^1$	$^2S_{1/2}$
5 B	[He] $2s^2 2p^1$	$^2P_{1/2}$	30 Zn	[Ar] $3d^{10} 4s^2$	$^1S_0$
6 C	[He] $2s^2 2p^2$	$^3P_0$	31 Ga	[Ar] $3d^{10} 4s^2 4p^1$	$^2P_{1/2}$
7 N	[He] $2s^2 2p^3$	$^4S_{3/2}$	32 Ge	[Ar] $3d^{10} 4s^2 4p^2$	$^3P_0$
8 O	[He] $2s^2 2p^4$	$^3P_2$	33 As	[Ar] $3d^{10} 4s^2 4p^3$	$^4S_{3/2}$
9 F	[He] $2s^2 2p^5$	$^2P_{3/2}$	34 Se	[Ar] $3d^{10} 4s^2 4p^4$	$^3P_2$
10 Ne	[He] $2s^2 2p^6$	$^1S_0$	35 Br	[Ar] $3d^{10} 4s^2 4p^5$	$^2P_{3/2}$
11 Na	[Ne] $3s^1$	$^2S_{1/2}$	36 Kr	[Ar] $3d^{10} 4s^2 4p^6$	$^1S_0$
12 Mg	[Ne] $3s^2$	$^1S_0$	37 Rb	[Kr] $5s^1$	$^2S_{1/2}$
13 Al	[Ne] $3s^2 3p^1$	$^2P_{1/2}$	38 Sr	[Kr] $5s^2$	$^1S_0$
14 Si	[Ne] $3s^2 3p^2$	$^3P_0$	39 Y	[Kr] $4d^1 5s^2$	$^2D_{3/2}$
15 P	[Ne] $3s^2 3p^3$	$^4S_{3/2}$	40 Zr	[Kr] $4d^2 5s^2$	$^3F_2$
16 S	[Ne] $3s^2 3p^4$	$^3P_2$	41 Nb	[Kr] $4d^4 5s^1$	$^6D_{1/2}$
17 Cl	[Ne] $3s^2 3p^5$	$^2P_{3/2}$	42 Mo	[Kr] $4d^5 5s^1$	$^7S_3$
18 Ar	[Ne] $3s^2 3p^6$	$^1S_0$	43 Tc	[Kr] $4d^5 5s^2$	$^6S_{5/2}$
19 K	[Ar] $4s^1$	$^2S_{1/2}$	44 Ru	[Kr] $4d^7 5s^1$	$^5F_5$
20 Ca	[Ar] $4s^2$	$^1S_0$	45 Rh	[Kr] $4d^8 5s^1$	$^4F_{9/2}$
21 Sc	[Ar] $3d^1 4s^2$	$^2D_{3/2}$	46 Pd	[Kr] $4d^{10}$	$^1S_0$
22 Ti	[Ar] $3d^2 4s^2$	$^3F_2$	47 Ag	[Kr] $4d^{10} 5s^1$	$^2S_{1/2}$
23 V	[Ar] $3d^3 4s^2$	$^4F_{3/2}$	48 Cd	[Kr] $4d^{10} 5s^2$	$^1S_0$
24 Cr	[Ar] $3d^5 4s^1$	$^7S_3$	49 In	[Kr] $4d^{10} 5s^2 5p^1$	$^2P_{1/2}$
25 Mn	[Ar] $3d^5 4s^2$	$^6S_{5/2}$	50 Sn	[Kr] $4d^{10} 5s^2 5p^2$	$^3P_0$

51	Sb	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>3</sup>	<sup>4</sup> S <sub>3/2</sub>	78	Pt	[Xe] 4f <sup>14</sup> 5d <sup>9</sup> 6s <sup>1</sup>	<sup>3</sup> D <sub>3</sub>
52	Te	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>4</sup>	<sup>3</sup> P <sub>2</sub>	79	Au	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>1</sup>	<sup>2</sup> S <sub>1/2</sub>
53	I	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>5</sup>	<sup>2</sup> P <sub>3/2</sub>	80	Hg	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup>	<sup>1</sup> S <sub>0</sub>
54	Xe	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>6</sup>	<sup>1</sup> S <sub>0</sub>	81	Tl	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>1</sup>	<sup>2</sup> P <sub>1/2</sub>
55	Cs	[Xe] 6s <sup>1</sup>	<sup>2</sup> S <sub>1/2</sub>	82	Pb	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup>	<sup>3</sup> P <sub>0</sub>
56	Ba	[Xe] 6s <sup>2</sup>	<sup>1</sup> S <sub>0</sub>	83	Bi	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>3</sup>	<sup>4</sup> S <sub>3/2</sub>
57	La	[Xe] 5d <sup>1</sup> 6s <sup>2</sup>	<sup>2</sup> D <sub>3/2</sub>	84	Po	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>4</sup>	<sup>3</sup> P <sub>2</sub>
58	Ce	[Xe] 4f <sup>1</sup> 5d <sup>1</sup> 6s <sup>2</sup>	<sup>1</sup> G <sub>4</sub>	85	At	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>5</sup>	<sup>2</sup> P <sub>3/2</sub>
59	Pr	[Xe] 4f <sup>3</sup> 6s <sup>2</sup>	<sup>4</sup> I <sub>9/2</sub>	86	Rn	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>6</sup>	<sup>1</sup> S <sub>0</sub>
60	Nd	[Xe] 4f <sup>4</sup> 6s <sup>2</sup>	<sup>5</sup> I <sub>4</sub>	87	Fr	[Rn] 7s <sup>1</sup>	<sup>2</sup> S <sub>1/2</sub>
61	Pm	[Xe] 4f <sup>5</sup> 6s <sup>2</sup>	<sup>6</sup> H <sub>5/2</sub>	88	Ra	[Rn] 7s <sup>2</sup>	<sup>1</sup> S <sub>0</sub>
62	Sm	[Xe] 4f <sup>6</sup> 6s <sup>2</sup>	<sup>7</sup> F <sub>0</sub>	89	Ac	[Rn] 6d <sup>1</sup> 7s <sup>2</sup>	<sup>2</sup> D <sub>3/2</sub>
63	Eu	[Xe] 4f <sup>7</sup> 6s <sup>2</sup>	<sup>8</sup> S <sub>7/2</sub>	90	Th	[Rn] 6d <sup>2</sup> 7s <sup>2</sup>	<sup>3</sup> F <sub>2</sub>
64	Gd	[Xe] 4f <sup>7</sup> 5d <sup>1</sup> 6s <sup>2</sup>	<sup>9</sup> D <sub>2</sub>	91	Pa	[Rn] 5f <sup>2</sup> 6d <sup>1</sup> 7s <sup>2</sup>	<sup>4</sup> K <sub>11/2</sub>
65	Tb	[Xe] 4f <sup>9</sup> 6s <sup>2</sup>	<sup>6</sup> H <sub>15/2</sub>	92	U	[Rn] 5f <sup>3</sup> 6d <sup>1</sup> 7s <sup>2</sup>	<sup>5</sup> L <sub>6</sub>
66	Dy	[Xe] 4f <sup>10</sup> 6s <sup>2</sup>	<sup>5</sup> I <sub>8</sub>	93	Np	[Rn] 5f <sup>4</sup> 6d <sup>1</sup> 7s <sup>2</sup>	<sup>6</sup> L <sub>11/2</sub>
67	Ho	[Xe] 4f <sup>11</sup> 6s <sup>2</sup>	<sup>4</sup> I <sub>15/2</sub>	94	Pu	[Rn] 5f <sup>6</sup> 7s <sup>2</sup>	<sup>7</sup> F <sub>0</sub>
68	Er	[Xe] 4f <sup>12</sup> 6s <sup>2</sup>	<sup>3</sup> H <sub>6</sub>	95	Am	[Rn] 5f <sup>7</sup> 7s <sup>2</sup>	<sup>8</sup> S <sub>7/2</sub>
69	Tm	[Xe] 4f <sup>13</sup> 6s <sup>2</sup>	<sup>2</sup> F <sub>7/2</sub>	96	Cm	[Rn] 5f <sup>7</sup> 6d <sup>1</sup> 7s <sup>2</sup>	<sup>9</sup> D <sub>2</sub>
70	Yb	[Xe] 4f <sup>14</sup> 6s <sup>2</sup>	<sup>1</sup> S <sub>0</sub>	97	Bk	[Rn] 5f <sup>8</sup> 6d <sup>1</sup> 7s <sup>2</sup>	<sup>8</sup> H <sub>17/2</sub>
71	Lu	[Xe] 4f <sup>14</sup> 5d <sup>1</sup> 6s <sup>2</sup>	<sup>2</sup> D <sub>3/2</sub>	98	Cf	[Rn] 5f <sup>10</sup> 7s <sup>2</sup>	<sup>5</sup> I <sub>8</sub>
72	Hf	[Xe] 4f <sup>14</sup> 5d <sup>2</sup> 6s <sup>2</sup>	<sup>3</sup> F <sub>2</sub>	99	Es	[Rn] 5f <sup>11</sup> 7s <sup>2</sup>	<sup>4</sup> I <sub>15/2</sub>
73	Ta	[Xe] 4f <sup>14</sup> 5d <sup>3</sup> 6s <sup>2</sup>	<sup>4</sup> F <sub>3/2</sub>	100	Fm	[Rn] 5f <sup>12</sup> 7s <sup>2</sup>	<sup>3</sup> H <sub>6</sub>
74	W	[Xe] 4f <sup>14</sup> 5d <sup>4</sup> 6s <sup>2</sup>	<sup>5</sup> D <sub>0</sub>	101	Md	[Rn] 5f <sup>13</sup> 7s <sup>2</sup>	<sup>2</sup> F <sub>7/2</sub>
75	Re	[Xe] 4f <sup>14</sup> 5d <sup>5</sup> 6s <sup>2</sup>	<sup>6</sup> S <sub>5/2</sub>	102	No	[Rn] 5f <sup>14</sup> 7s <sup>2</sup>	<sup>1</sup> S <sub>0</sub>
76	Os	[Xe] 4f <sup>14</sup> 5d <sup>6</sup> 6s <sup>2</sup>	<sup>5</sup> D <sub>4</sub>	103	Lr	[Rn] 5f <sup>14</sup> 6d <sup>1</sup> 7s <sup>2</sup>	
77	Ir	[Xe] 4f <sup>14</sup> 5d <sup>7</sup> 6s <sup>2</sup>	<sup>4</sup> F <sub>9/2</sub>	104	Rf	[Rn] 5f <sup>14</sup> 6d <sup>2</sup> 7s <sup>2</sup>	

LS terms for electron configurations p<sup>2</sup> and p<sup>3</sup>

$$p^2: {}^3P (9), {}^1D (5), {}^1S (1) \quad \binom{6}{2} = 15 = 9 + 5 + 1$$

$$p^3: {}^4S (4), {}^2D (10), {}^2P (6) \quad \binom{6}{3} = 20 = 4 + 10 + 6$$

Energy levels of neutral tetravalent atoms from the p-, d-, and f-block (C, Ti, Ce), within an energy range above lowest ground state level:

$$\Delta E = 1 \text{ eV} \approx 8065.55 \text{ cm}^{-1} \quad (E_h = 2 h c R_\infty)$$

Energy levels of C I<sup>‡‡</sup> (280 lines of data) — IP = 11.26030 eV

Configuration	Term	J	Level (cm <sup>-1</sup> )				
2s2.2p2	3P	0	0.00	2s2.2p(2P*)26d	1F*	3	90721.0
		1	16.40	2s2.2p(2P*)27d	1F*	3	90732.7
		2	43.40	2s2.2p(2P*)28d	1F*	3	90742.2
2s2.2p2	1D	2	10192.63	2s2.2p(2P*)29d	1F*	3	90753.8
2s2.2p2	1S	0	21648.01				
2s.2p3	5S*	2	33735.20				
2s2.2p(2P*)3s	3P*	0	60333.43	C II (2P*<1/2>)	Limit		90820.42
		1	60352.63	C II (2P*<3/2>)	Limit		90883.84
		2	60393.14				
2s2.2p(2P*)3s	1P*	1	61981.82	2s.2p2(4P)3s	5P	1	103541.8
2s.2p3	3D*	3	64086.92			2	103562.5
		1	64089.85			3	103587.3
		2	64090.95	2s.2p3	3S*	1	105798.7
				2s.2p3	1P*	1	[119878]

‡‡ Source: Atomic Spectra Database, <http://physics.nist.gov/PhysRefData/contents.html>

Energy levels of Ti I<sup>‡‡</sup> (380 lines of data) — IP = 6.820 eV

Configuration	Term	J	Level (cm <sup>-1</sup> )	Lande g	Leading Percentages	
3d2.4s2	a 3F	2	0.000	0.66	100	
		3	170.132	1.08	100	
		4	386.874	1.25	100	
3d3(4F)4s	a 5F	1	6556.828	0.00	100	
		2	6598.749	0.99	100	
		3	6661.003	1.25	100	
		4	6742.757	1.35	100	
		5	6842.964	1.41	100	
3d2.4s2	a 1D	2	7255.369	1.02	96	2 3d3.(2D2).4s 1D
3d2.4s2	a 3P	0	8436.618		92	7 3d3.(2P).4s 3P
		1	8492.421	1.50	92	7 3d3.(2P).4s 3P
		2	8602.340	1.49	90	7 3d3.(2P).4s 3P
3d3(4F)4s	b 3F	2	11531.760	0.67	100	
		3	11639.804	1.08	100	
		4	11776.806	1.26	98	1 3d2.3s2 1G

‡‡ Source: Atomic Spectra Database, <http://physics.nist.gov/PhysRefData/contents.html>

Energy levels of Ti I (contd.)

3d2.4s2	a 1G	4	12118.394	0.98	90	8 3d3.(2G).4s 1G
			⋮	⋮	⋮	
3d4	a 5D	0	28772.86		100	
		1	28791.62		100	
		2	28828.51		100	
		3	28882.44		100	
		4	28952.10		100	
			⋮	⋮	⋮	
3d2.4p2	e 3D	2	48724.34			
		1	48724.83			
		3	48839.74			
3d2.4p2	h 5D	0	48802.32			
		1	48859.51			
		2	48915.07			
		3	49024.43			
		4	49036.46			

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Energy levels of Ti I (contd.)

	f 3D	2	49571.69		
		3	49619.72		
	f 1D	2	50128.08		
	f 1G	4	52125.98		
	e 1P	1	53663.32		
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Ti II (4F<3/2>)	Limit		55010		

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Energy levels of Ce I<sup>‡‡</sup> (953 lines of data) — IP = 5.5386 eV

Configuration	Term	J	Level (cm <sup>-1</sup> )	Lande g	Leading Percentages
4f.5d 6s2	1G*	4	0.000	0.94543	55 29 3H*
4f.5d 6s2	3F*	2	228.849	0.76515	66 24 1D*
		3	1663.120	1.07736	85 7 4f(2F*).5d2(1D).6s(2D) 3F*
		4	3100.151*	1.07703	34 27 4f(2F*).5d2(3F).6s(4F) 5I*
4f.5d 6s2	3H*	4	1279.424	0.88979	54 20 1G*
		5	2208.657	1.03212	80 12 4f(2F*).5d2(1D).6s(2D) 3H*
		6	3976.104	1.16032	78 13 4f(2F*).5d2(1D).6s(2D) 3H*
4f.5d 6s2	3G*	3	1388.941	0.73494	66 11 4f(2F*).5d2(1D).6s(2D) 3G*
		5	4199.367	1.15021	48 34 4f(2F*).5d2(3F).6s(4F) 5H*
4f(2F*) 5d2(3F)6s (4F)	5H*	3	2369.068	0.59978	66 16 4f.5d.6s2 3G*
		4	2437.629	0.98592	38 25 (2F*) (3F)(4F) 3G*
		6	4746.627	1.16593	67 24 (2F*) (3F)(4F) 5I*
		7	5802.108	1.237	62 38 (2F*) (3F)(4F) 5I*
4f.5d 6s2	1D*	2	2378.827	0.93654	54 23 3F*

‡‡ Source: Atomic Spectra Database, <http://physics.nist.gov/PhysRefData/contents.html>

Energy levels of Ce I (contd.)

4f(2F*) 5d2(3F)6s (4F)	5I*	4	3196.607	0.66612	67 11 4f.5d.6s2 3F*
		5	3764.008	0.90691	90 3 4f.5d.6s2 3H*
		6	4455.756	1.11714	64 26 (2F*) (3F)(4F) 5H*
		7	5315.803	1.21625	56 33 (2F*) (3F)(4F) 5H*
		8	6809.128	1.250	100
4f(2F*) 5d2(3F)6s (4F)	*	5	3210.583	1.16277	41 3G* 37 (2F*) (3F)(4F) 5H*
4f.5d 6s2	*	4	3312.240*	1.08582	29 3F* 26 3G*
4f.5d 6s2	3D*	1	3710.513	0.61549	64 10 4f(2F*).5d2(1D).6s(2D) 3D*
		2	4766.323	1.14945	67 12 4f(2F*).5d2(1D).6s(2D) 3D*
		3	5006.719	1.23674	58 20 1F*
4f(2F*) 5d2(3F)6s (4F)	*	0	3974.503		29 5D* 23 (2F*) (1D)(2D) 3P*
4f(2F*) 5d2(3F)6s (4F)	*	1	4020.954	1.49404	17 3S* 15 (2F*) (1D)(2D) 3P*
4f(2F*) 5d2(3F)6s (4F)	3G*	3	4160.283	0.72933	47 23 (2F*) (3F)(4F) 5H*
4f(2F*) 5d2(3F)6s (4F)	*	4	4173.494	1.02948	41 3G* 30 (2F*) (3F)(4F) 5H*
4f(2F*) 5d2(3F)6s (4F)	*	5	4417.618	1.17790	29 3G* 28 4f.5d.6s2 3G*

## Energy levels of Ce I (contd.)

4f2.6s2	3H	4	4762.718	0.80508	89	4 4f.5d(3G*).6s.6p(1P*) 3H
		5	6238.934	1.035	92	4 4f.5d(3G*).6s.6p(1P*) 3H
		6	7780.202	1.169	92	4 4f.5d(3G*).6s.6p(1P*) 3H
4f(2F*) 5d2(3F)6s (4F)	3S*	1	5097.777	1.88257	49	25 (2F*) (3F)(4F) 5D*
4f(2F*) 5d2(3F)6s (4F)	*	2	5210.906	1.22694	28 5D*	27 (2F*) (3F)(4F) 5G*
4f(2F*) 5d2(3F)6s (4F)	5G*	2	5409.236	0.773	35	24 (2F*) (3F)(4F) 5D*
		3	6234.792	1.04965	69	13 (2F*) (3F)(4F) 5D*
		4	6856.559	1.150	72	6 (2F*) (3F)(2F) 1G*
		5	7467.160	1.179	69	7 (2F*) (3F)(4F) 3H*
		6	8055.526	1.207	50	18 (2F*) (3F)(4F) 3H*
4f(2F*) 5d2(3F)6s (4F)	*	3	5519.751	1.24530	32 5D*	21 (2F*) (3F)(4F) 3F*
4f(2F*) 5d2(3F)6s (4F)	*	0	5571.156		44 5D*	35 4f.5d.6s2 3P*
4f(2F*) 5d2(3F)6s (4F)	*	4	5572.074	1.31658	29 5D*	27 (2F*) (3F)(4F) 3F*
4f.5d 6s2	*	1	5637.233	1.389	30 3P*	26 4f(2F*).5d2(3F).6s(4F) 5D*
4f(2F*) 5d2(3F)6s (4F)	5F*	1	5674.829	0.140	73	6 (2F*) (3F)(4F) 5D*
		2	5904.006	0.905	66	13 (2F*) (3F)(4F) 5G*
		3	6337.061	1.232	42	16 (2F*) (3F)(4F) 5D*
		4	7174.156	1.373	67	19 (2F*) (3F)(4F) 5D*
		5	7933.558	1.345	81	5 (2F*) (3P)(4P) 5F*

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## Energy levels of Ce I (contd.)

4f.5d 6s2	*	2	6303.984	1.419	36 3P*	16 4f(2F*).5d2(1D).6s(2D) 3P*
4f(2F*) 5d2(3F)6s (2F)	*	4	6475.540	0.897	43 3H*	17 (2F*)(3F)(2F) 1G*
4f.5d 6s2	*	3	6621.892	1.147	35 1F*	17 3D*
4f(2F*) 5d2(3F)6s (4F)	*	5	6663.226	0.953	19 3I*	18 (2F*)(3F)(2F) 3I*
4f(2F*) 5d2(3F)6s (4F)	*	2	6836.628	0.68078	33 3F*	18 (2F*)(3F)(4F) 5G*
4f(2F*) 5d2(3F)6s (4F)	*	3	7169.751	1.13	28 3F*	26 (2F*)(3F)(4F) 5F*
4f(2F*) 5d2(3F)6s (2F)	*	4	7348.299	0.964	22 1G*	21 (2F*)(3F)(4F) 3H*
4f(2F*) 5d2(3F)6s (4F)	*	6	7696.210	1.076	39 3I*	19 (2F*)(1G)(2G) 3I*
4f(2F*) 5d2(3F)6s (4F)?	*	5	7715.236	0.934	22 3I*	14 (2F*)(3F)(4F) 5G*
4f(2F*) 5d2(3F)6s (2F)?	*	5	7841.955	1.063	24 3H*	21 (2F*)(3F)(2F) 3I*
4f(2F*) 5d2(1D)6s (2D)	*	1	7853.119	0.983	27 1P*	16 (2F*)(3F)(2F) 3D*
4f(2F*) 5d2(3F)6s (4F)	*	4	7890.429	1.242	25 3F*	18 (2F*)(3F)(4F) 5D*

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Energy levels of Ce I (contd.)

4f(2F*) 5d2(3P)6s (4P)	5G*	2	8088.912	0.403	95	3 (2F*)(3F)(4F) 5G*
		3	8307.309	0.957	81	6 (2F*)(3P)(4P) 3G*
		4	8762.126	1.054	50	9 (2F*)(3F)(2F) 3H*
		5	9462.705	1.19	46	12 (2F*)(3P)(4P) 3G*
		6	11030.470	1.193	51	21 (2F*)(3F)(2F) 3H*
4f(2F*) 5d2(3F)6s (4F)	5P*	2	8101.187	1.735	85	5 (2F*)(3F)(4F) 5S*
		3	8270.249	1.504	74	11 (2F*)(3F)(4F) 3D*
		1	8430.846	2.04	62	10 (2F*)(3F)(4F) 3P*
4f2.6s2	3F	2	8235.605	0.680	88	4 4f.5d(3F*).6s.6p(1P*) 3F
		3	9206.305	1.083	90	4 4f.5d(3F*).6s.6p(1P*) 3F
		4	9379.148	1.139	55	32 1G
4f(2F*) 5d2(3F)6s (2F)	1S*	0	8351.167		44	17 4f.5d.6s2 3P*
4f(2F*) 5d2(3F)6s (4F)	*	2	8366.098	1.525	33 3P*	16 (2F*)(3F)(4F) 5S*
4f(2F*) 5d2(3F)6s (2F)	*	5	8400.730	0.917	30 3I*	19 4f.5d.6s2 1H*
4f(2F*) 5d2(3F)6s (2F)	*	4	8509.209	0.954	20 3H*	19 (2F*)(3P)(4P) 5G*
4f(2F*) 5d2(3F)6s (4F)	3I*	7	8587.973	1.155	59	24 (2F*)(1G)(2G) 3I*
4f(2F*) 5d2(3F)6s (4F)	*	6	8603.531	1.225	36 5G*	25 (2F*)(3F)(4F) 3H*

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Energy levels of Ce I (contd.)

4f(2F*) 5d2(3F)6s (4F)	*	1	8695.201	1.285	22 3P*	12 (2F*)(3F)(4F) 5P*
4f(2F*) 5d2(3F)6s (2F)	*	3	8902.306	1.128	20 1F*	14 4f.5d.6s2 1F*
4f(2F*) 5d2(3F)6s (2F)	*	5	8991.451	1.067	31 3H*	17 (2F*)(3P)(4P) 5G*
4f(2F*) 5d2(3F)6s (4F)	*	0	9119.094		40 3P*	32 (2F*)(3F)(2F) 1S*
4f(2F*) 5d2(3P)6s (4P)	3D*	3	9135.099	1.274	50	12 (2F*)(3F)(4F) 5P*
4f(2F*) 5d2(3F)6s (2F)	*	2	9200.707	1.376	24 3D*	21 (2F*)(3P)(2P) 3D*
4f(2F*) 5d2(3F)6s (2F)	3I*	6	9333.222	1.047	61	20 (2F*)(1G)(2G) 3I*
		7	11061.551	1.141	79	16 (2F*)(1G)(2G) 3I*
4f(2F*) 5d2(3F)6s (4F)	*	1	9369.628	1.065	21 3P*	17 (2F*)(3F)(2F) 3D*
4f(2F*) 5d2(3P)6s (4P)	3D*	2	9425.529	1.207	46	8 (2F*)(3F)(4F) 5S*
4f(2F*) 5d2(3F)6s (2F)	3F*	2	9709.012	0.799	51	13 (2F*)(3P)(2P) 3F*
4f(2F*) 5d2(3F)6s (2F)?	3G*	3	9787.220	0.868	42	26 (2F*)(3P)(2P) 3G*

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Energy levels of Ce I (contd.)

		∴	∴	∴
*	6	30603.359		
*	4,3	30624.042		
*	2	30706.313		
*	4	30739.270		
*	3	30740.884		
*	5	30767.047		
*	4	30787.639	0.695?	
*	3	30854.052	0.737	
*	7	30876.234		
*	2	30991.841		
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Ce II (4H* $\langle 7/2 \rangle$ )	Limit	44672		

H atom in a weak homogeneous electric field (Stark effect) — perturbation theory