PHY 742 Quantum Mechanics II
12-12:50 PM MWF Olin 103

Plan for Lecture 29

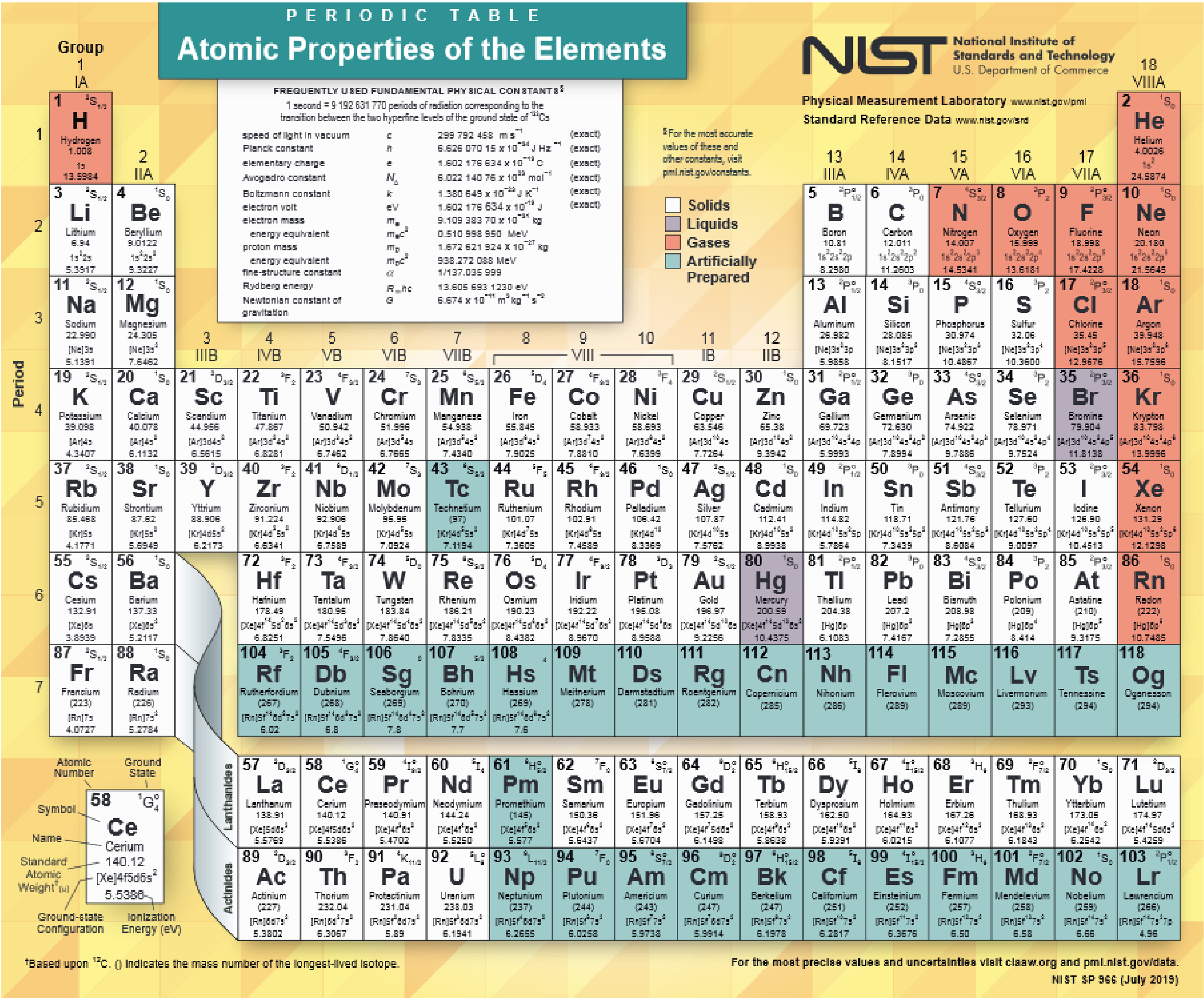
Quantum mechanics of a multi electron atom

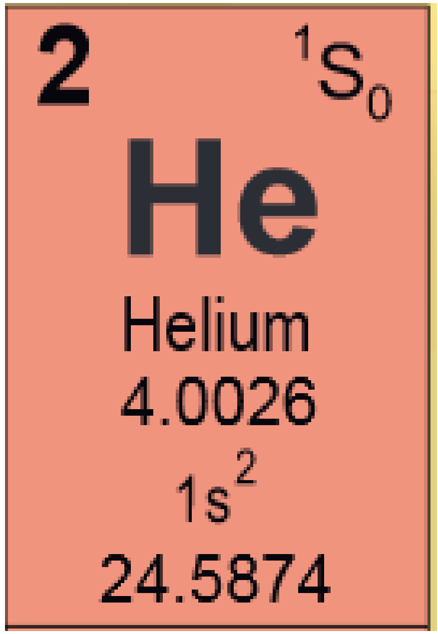
Analysis of atomic term splittings

1. Energy of closed shells
2. 1 electron outside a closed shell
3. 2 electrons outside a closed shell

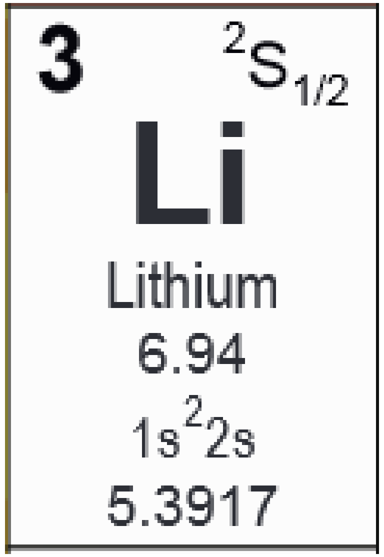
25	Mon: 04/04/2022	Chap. 10 (review)	Multiparticle systems and second quantization	#20	04/06/2022
26	Wed: 04/06/2022	Chap. 10 (review)	Multiparticle systems and second quantization		
27	Fri: 04/08/2022		Multi electron atoms	#21	04/11/2022
28	Mon: 04/11/2022		Multi electron atoms	#22	04/18/2022
29	Wed: 04/13/2022		Multi electron atoms		
	Fri: 04/15/2022	*No class*	Holiday		
30	Mon: 04/18/2022		Hubbard model with multiple electrons		
31	Wed: 04/20/2022		BCS model of superconductivity		
32	Fri: 04/22/2022		BCS model of superconductivity		

https://www.nist.gov/pml/periodic-table-elements

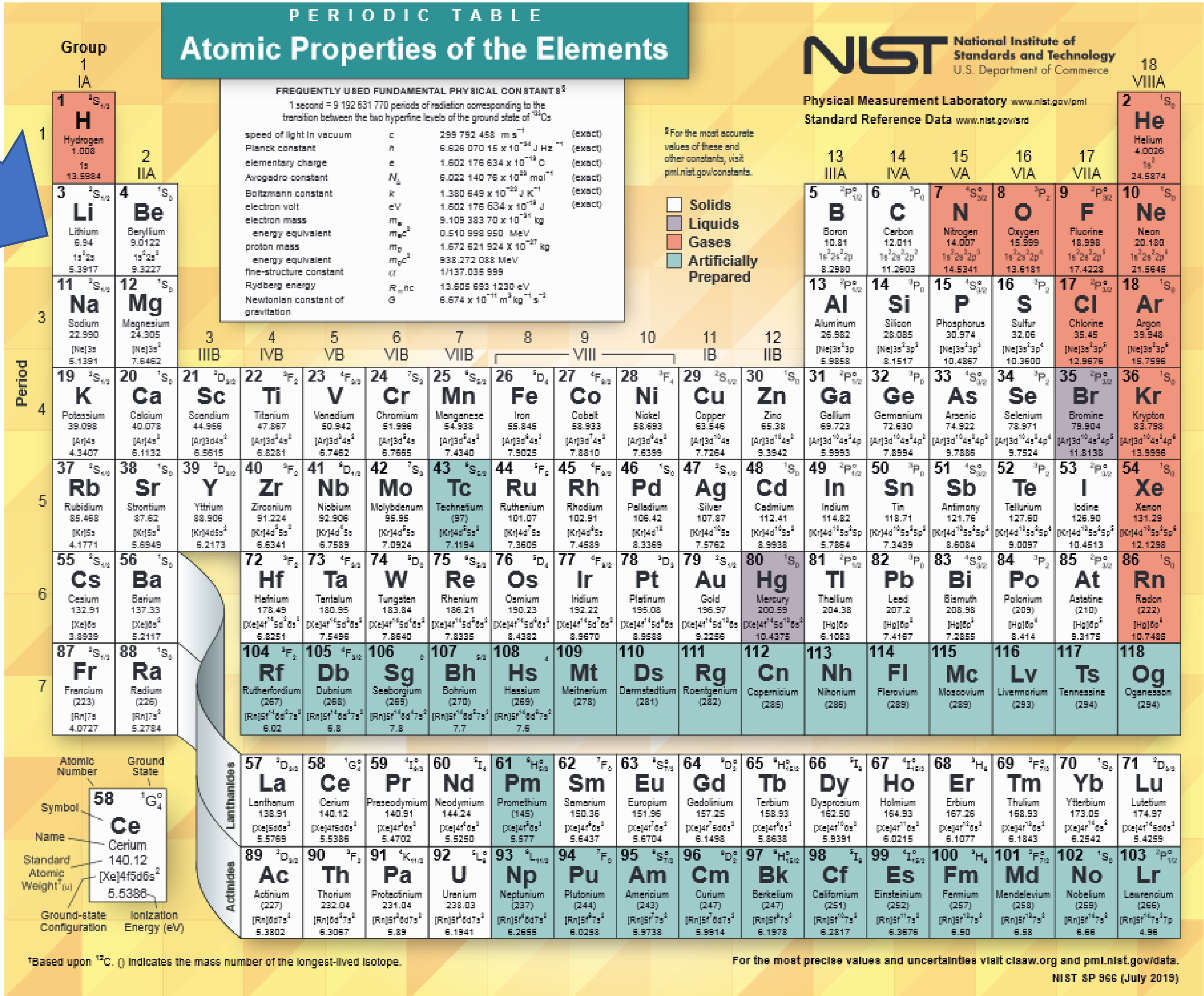


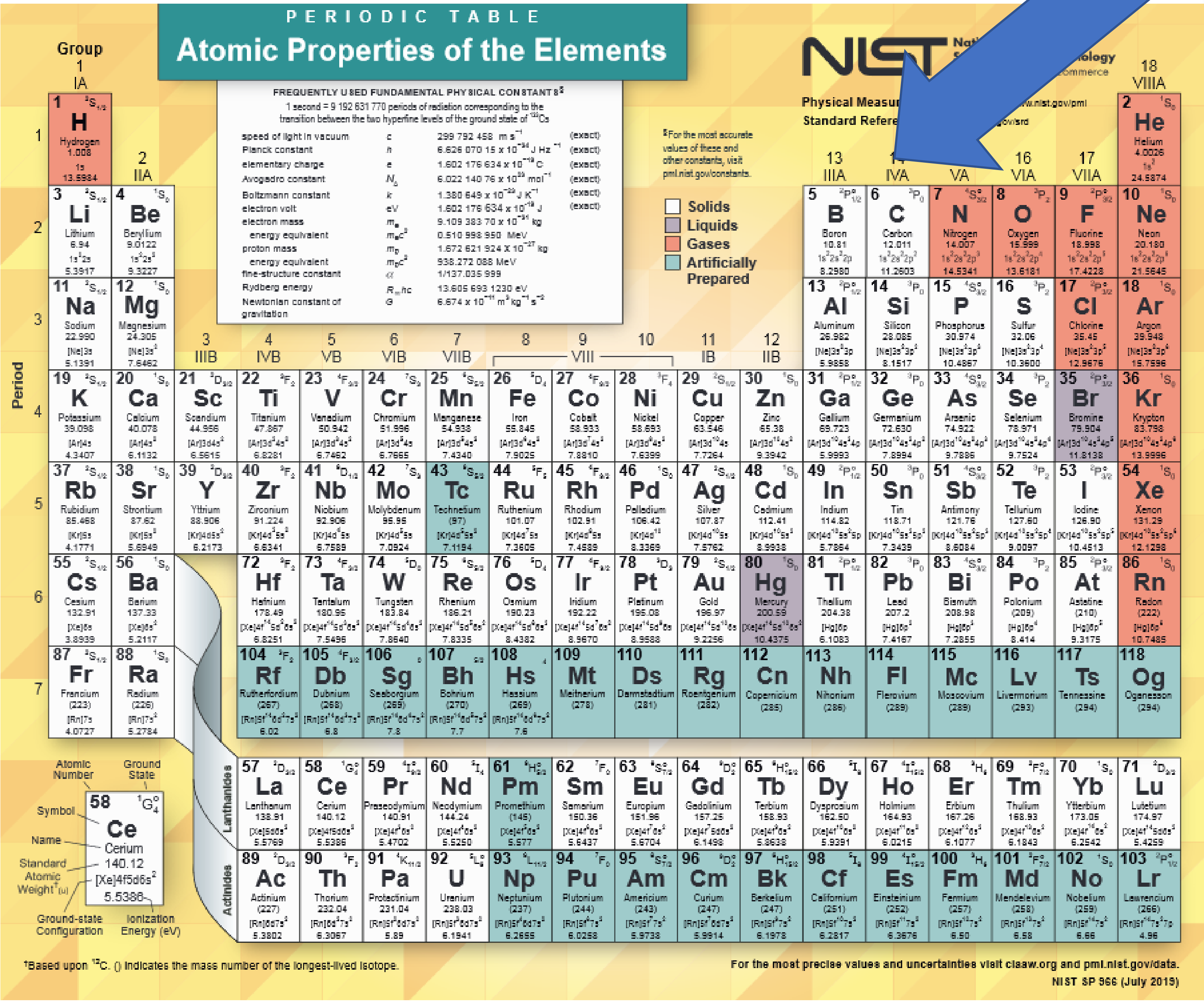


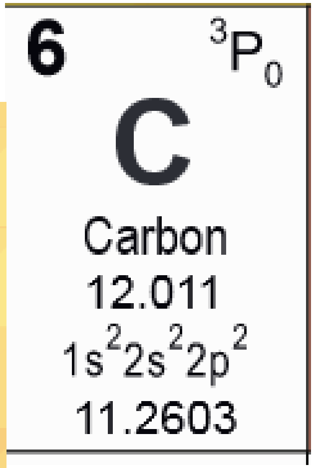
Closed shell



One electron outside a closed shell

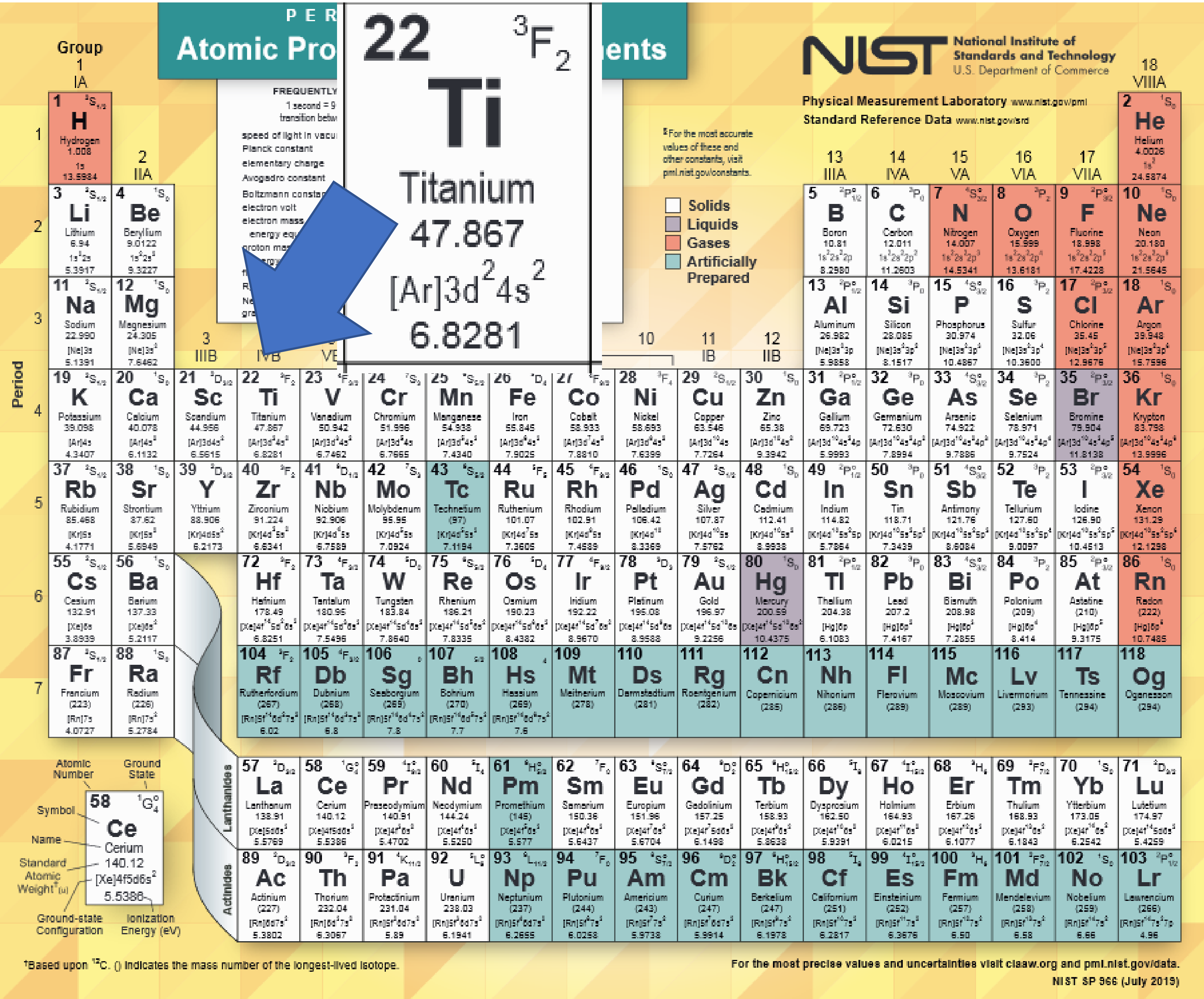






2 electrons outside a closed shell

2 electrons outside a closed shell



In this discussion, we focus our attention on the multiplet structures of atoms in their ground states, where the zero order structure is described in terms of the single particle Hamiltonian. For this discussion, the single particle Hamiltonian is a H-like ion with nuclear charge Z. As you can imagine, the numerical errors increase as Z increases. However, the qualitative features remain correct. The numerics can be improved by defining other single particle Hamiltonians. For example, density functional Hamiltonians work quite well in this context.

DEFINITION: Closed shell configuration means that for any given "shell" with orbital angular momentum quantum number *l*, there are *2(2l+1)* electrons occupying that shell. For example: ns^2 np^6 nd^{10} nf^{14}

General form Hamiltonian for *N*-electron atom

$$H(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) = \sum_{i=1}^{N} h(\mathbf{r}_i) + V(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$$

$$\text{where: } V(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) = \sum_{i=1\ (i>j)}^{N} \sum_{j=1}^{N} v(\mathbf{r}_i - \mathbf{r}_j)$$

Single particle basis: $\quad h(\mathbf{r})\varphi_k(\mathbf{r}) = \varepsilon_k \varphi_k(\mathbf{r})$

Matrix elements for electron interaction potential

$$v_{ijkl} \equiv \left\langle \varphi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_2) \middle| v(\mathbf{r}_1 - \mathbf{r}_2) \middle| \varphi_k(\mathbf{r}_1)\varphi_l(\mathbf{r}_2) \right\rangle$$

1 2

Hamiltonian in second quantization form:

$$H = \sum_i \varepsilon_i f_i^\dagger f_i + \sum_{ijkl} v_{ijkl} f_i^\dagger f_j^\dagger f_l f_k$$

Review of ground state of He atom (example of closed shell system)

The Hamiltonian for an He atom (Z=2): (cgs Gaussian units)

$$H(\mathbf{r}_1,\mathbf{r}_2) = -\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2) - 2e^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + \frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}$$

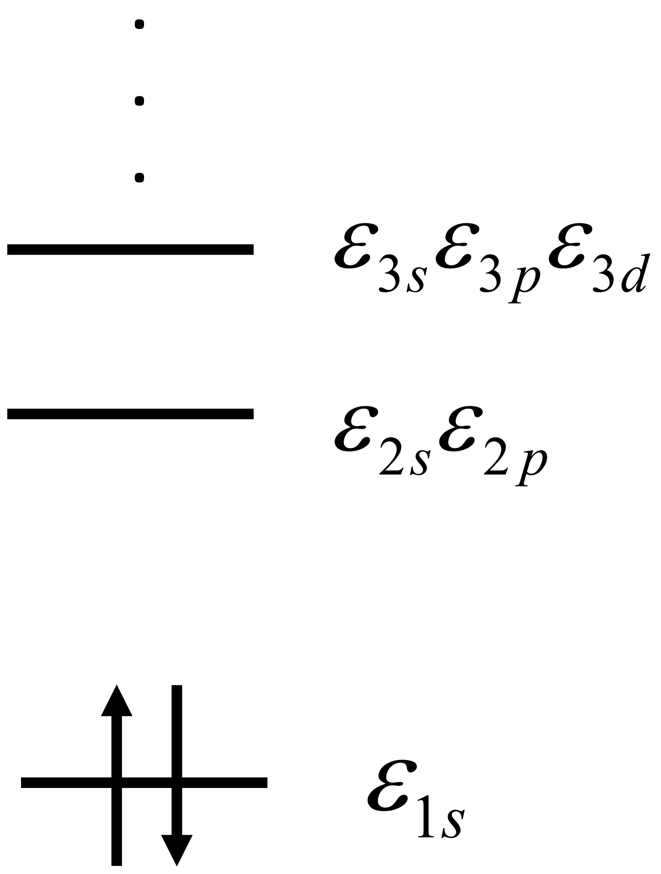
$$= \underbrace{-\frac{\hbar^2\nabla_1^2}{2m} - \frac{2e^2}{r_1}} \underbrace{-\frac{\hbar^2\nabla_2^2}{2m} - \frac{2e^2}{r_2}} + \frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}$$

$$= \qquad h(\mathbf{r}_1) \qquad + \qquad h(\mathbf{r}_2) \qquad + v(\mathbf{r}_1,\mathbf{r}_2)$$

Single particle basis:

$$h(\mathbf{r}_1)\varphi_a(\mathbf{r}_1) \equiv h(\mathbf{r}_1)\varphi_{nlmm_s}(\mathbf{r}_1) = \varepsilon_n\varphi_{nlmm_s}(\mathbf{r}_1)$$

Ground state configuration for He atom



$$\psi = f^{\dagger}_{1s\alpha} f^{\dagger}_{1s\beta} \left|0\right\rangle$$

Summary of results

$$H = \sum_i \varepsilon_i f_i^\dagger f_i + \sum_{ijkl} v_{ijkl} f_i^\dagger f_j^\dagger f_l f_k$$

Need to evaluate $\langle \psi | H | \psi \rangle$ for $\psi = f_{1s\alpha}^\dagger f_{1s\beta}^\dagger |0\rangle$

$$\langle \psi | H | \psi \rangle = 2\varepsilon_{1s} + v_{1s1s1s1s}$$

Note that in coordinate and spin representation,

$$\psi = \frac{1}{\sqrt{2}} \varphi_{1s}(\mathbf{r}_1) \varphi_{1s}(\mathbf{r}_2) \left(\alpha_1 \beta_2 - \alpha_2 \beta_1 \right)$$

Example from NIST

NIST Atomic Spectra Database Levels Data

He I 198 Levels Found

Z = 2, He isoelectronic sequence

Configuration	Term	*J*	Level (eV)
$1s^2$	^1S	0	0.00000000
$1s2s$	^3S	1	[19.81961468]
$1s2s$	^1S	0	[20.61577496]
$1s2p$	$^3P^o$	2	[20.96408703]
		1	[20.96409651]
		0	[20.96421899]
$1s2p$	$^1P^o$	1	[21.21802284]

https://physics.nist.gov/PhysRefData/ASD/levels_form.html

Example of atom with one electron outside complete shell

NIST Atomic Spectra Database Levels Data

Li I   182 Levels Found

Z = 3, Li isoelectronic sequence

Data on Landé factors and level compositions are not available for this ion in ASD

Some data for neutral and singly-charged ions are available in the Handbook of Basic Atomic Spectroscopic Data

Primary data source	
Unpublished level list prepared for line classifications published in Kelly 1987	These data are not critically evaluated by NI

Configuration	Term	J	Level (eV)	Uncertainty (eV)	Reference
$1s^2 2s$	^2S	$1/2$	0.000000	0.000012	L3462
$1s^2 2p$	$^2P^o$	$1/2$	*1.847818*	*0.000012*	
		$3/2$	*1.847860*	*0.000012*	
$1s^2 3s$	^2S	$1/2$	3.373129	0.000012	
$1s^2 3p$	$^2P^o$	$3/2$	*3.834258*	*0.000012*	

In order to analyze these atoms – we need to be able to evaluate the electron interactions

Electron-electron Coulomb repulsion:

$$v(\mathbf{r}_1-\mathbf{r}_2)=\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}=e^2\sum_{\lambda\mu}\frac{4\pi}{2\lambda+1}\frac{r_<^\lambda}{r_>^{\lambda+1}}Y_{\lambda\mu}(\hat{\mathbf{r}}_1)Y_{\lambda\mu}^*(\hat{\mathbf{r}}_2)$$

Define: $\mathcal{R}^\lambda(n_al_a,n_bl_b;n_cl_c,n_dl_d)=\int_0^\infty r_1^2dr_1\int_0^\infty r_2^2dr_2\,\frac{r_<^\lambda}{r_>^{\lambda+1}}R_{n_al_a}(r_1)R_{n_bl_b}(r_2)R_{n_cl_c}(r_1)R_{n_dl_d}(r_2)$

$$v_{abcd}\equiv\left\langle\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2)\middle|v(\mathbf{r}_1-\mathbf{r}_2)\middle|\varphi_c(\mathbf{r}_1)\varphi_d(\mathbf{r}_2)\right\rangle$$

$$=\sum_{\lambda\mu}\frac{e^2}{2\lambda+1}\mathcal{R}^\lambda(n_al_a,n_bl_b;n_cl_c,n_dl_d)G(l_a\overline{m}_a,\lambda\overline{\mu},l_cm_c)G(l_b\overline{m}_b,\lambda\mu,l_dm_d)(-1)^{m_a+\mu+m_b}$$

These angular terms have been tabulated by Condon and Shortley and others

Here, the angular integrals are given in terms of Gaunt Coefficients and 3j symbols:

$$\int_0^{2\pi}\int_0^{\pi} Y_{l_1,m_1}(\theta,\phi)Y_{l_2,m_2}(\theta,\phi)Y_{l_3,m_3}(\theta,\phi)\sin\theta\;\mathrm{d}\theta\;\mathrm{d}\phi$$

$$= \left(\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}\right)^{\frac{1}{2}} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}.$$

$$\equiv \frac{1}{\sqrt{4\pi}} G\left(l_1 m_1, l_2 m_2, l_3 m_3\right)$$

Note that $\quad Y^*_{lm}(\theta,\varphi) = (-1)^m Y_{l-m}(\theta,\varphi)$

Digression on angular relationships --

"Addition" of angular momentum

Clebsch-Gordan coefficients

$$\left|JM, j_1 j_2\right\rangle = \sum_{m_1, m_2} \left|j_1 m_1, j_2 m_2\right\rangle \left\langle j_1 m_1, j_2 m_2 \middle| JM, j_1 j_2\right\rangle$$

A more symmetric coefficient is the so-called 3-j symbol:

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

Clebsch-Gordan 3-j

$$\left(j_1\, m_1\, j_2\, m_2 \,|\, j_1\, j_2\, j_3\, m_3\right) = (-1)^{j_1 - j_2 + m_3} (2j_3 + 1)^{\frac{1}{2}} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{pmatrix}$$

link to more information: http://dlmf.nist.gov/34.1

Some symmetry properties of 3-j symbols:

$$|j_r - j_s| \le j_t \le j_r + j_s,$$

$$m_1 + m_2 + m_3 = 0\,.$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_3 & j_1 \\ m_2 & m_3 & m_1 \end{pmatrix} = \begin{pmatrix} j_3 & j_1 & j_2 \\ m_3 & m_1 & m_2 \end{pmatrix},$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix}.$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix},$$

Some orthogonality properties of 3-j symbols:

$$\sum_{m_1 m_2} (2j_3+1)\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}\begin{pmatrix} j_1 & j_2 & j_3' \\ m_1 & m_2 & m_3' \end{pmatrix} = \delta_{j_3,j_3'}\delta_{m_3,m_3'},$$

$$\sum_{j_3 m_3} (2j_3+1)\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1' & m_2' & m_3 \end{pmatrix} = \delta_{m_1,m_1'}\delta_{m_2,m_2'},$$

$$\sum_{m_1 m_2 m_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = 1\,.$$

Relationship of 3-j symbols to integrals over spherical harmonics and related functions

$$\int_0^{\pi} P_{l_1}(\cos\theta)P_{l_2}(\cos\theta)P_{l_3}(\cos\theta)\sin\theta\,\mathrm{d}\theta = 2\begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix}^2,$$

Gaunt Coefficient

$$\int_0^{2\pi}\int_0^{\pi} Y_{l_1,m_1}(\theta,\phi)Y_{l_2,m_2}(\theta,\phi)Y_{l_3,m_3}(\theta,\phi)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$

$$= \left(\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}\right)^{\frac{1}{2}}\begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}.$$

$$\equiv \frac{1}{\sqrt{4\pi}} G\left(l_1m_1, l_2m_2, l_3m_3\right)$$

Explicit formula for Clebsch-Gordon coefficients:

Reference: Abramowitz & Stegum – pg. 1006

Original formula:

$$\langle j_1 j_2 m_1 m_2 | j_1 j_2 j m\rangle = \delta_{m,m_1+m_2}\sqrt{\frac{(j_1+j_2-j)!(j_1-j_2+j)!(-j_1+j_2+j)!(2j+1)}{(j_1+j_2+j+1)!}}$$
$$\times \sum_k \frac{(-1)^k\sqrt{(j_1+m_1)!(j_1-m_1)!(j_2+m_2)!(j_2-m_2)!(j+m)!(j-m)!}}{k!(j_1+j_2-j-k)!(j_1-m_1-k)!(j_2+m_2-k)!(j-j_2+m_1+k)!(j-j_1-m_2+k)!}$$

Working formula:

$$\langle j_1 j_2 m_1 m_2 | j_1 j_2 j m\rangle = \delta_{m,m_1+m_2}\sqrt{\frac{(j_1-j_2+j)!(-j_1+j_2+j)!(2j+1)}{(j_1+j_2-j)!(j_1+j_2+j+1)!}}$$
$$\times\sqrt{\frac{(j_1+m1)!(j_2-m_2)!(j+m)!}{(j_1-m1)!(j_2+m_2)!(j-m)!}}$$
$$\times \sum_k \frac{(-1)^k}{k!}\frac{(j_1+j_2-j)!}{(j_1+j_2-j-k)!}\frac{(j_1-m_1)!}{(j_1-m_1-k)!}\frac{(j_2+m_2)!}{(j_2+m_2-k)!}\frac{(j-m)!}{(j-j_2+m_1+k)!(j-j_1-m_2+k)!}$$

Coupling of orbital angular momenta of multiple electrons

$$\mathbf{J} = \mathbf{L_1} + \mathbf{L_2}$$

$$J = |l_1 - l_2|, |l_1 - l_2| + 1, ..., (l_1 + l_2)$$

Example: $l_1 = l_2 = 1$ total of 9 orbital states

$J = 0$ 1 state

$J = 1$ 3 states

$J = 2$ 5 states

Consequences of orbital coupling on energies of multi-electron atoms

Example C $1s^2\ 2s^2\ 2p^2$

https://physics.nist.gov/PhysRefData/ASD/levels_form.html

Primary data source	Query NIST Bibliographic Database for **C I** (new window)
Moore 1993	Literature on C I Energy Levels

Configuration	Term	J	Level (eV)	Reference
$2s^22p^2$	^3P	0	0.00000	L7288
		1	0.002033	
		2	0.005381	
$2s^22p^2$	^1D	2	1.263725	
$2s^22p^2$	^1S	0	2.684011	

Atomic term notation: $$^{(2S+1)}L_J$$

For the example of the single particle configuration

np^2

L	*symbol*	*spin for 2 electrons*
0	*S*	*S=0*
1	*P*	*S=1*
2	*D*	*S=0*

In this case, it happens that L+S=even

why?

Example for C $1s^2$ $2s^2$ $2p^2$

States of total orbital momentum: $(2l_1+1)(2l_2+1)=9$

Total number of orbital and spin configurations: $6 \cdot 5/2 = 15$

${}^1D \Rightarrow 5$ states

${}^1S \Rightarrow 1$ states

${}^3P \Rightarrow 9$ states

Energetic differences are due to the electron-electron Coulomb repulsion:

$$v(\mathbf{r}_1 - \mathbf{r}_2) = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} = e^2 \sum_{\lambda\mu} \frac{4\pi}{2\lambda+1} \frac{r_<^\lambda}{r_>^{\lambda+1}} Y_{\lambda\mu}(\hat{\mathbf{r}}_1) Y_{\lambda\mu}^*(\hat{\mathbf{r}}_2)$$

Example for ^1D state

$$\left|JM;l_1l_2\right\rangle = \left|22;11\right\rangle = \sum_{m_1,m_2}\left|l_1m_1,l_2m_2\right\rangle\left\langle l_1m_1,l_2m_2\right|JM;l_1l_2\right\rangle$$

$$=\left|11,11\right\rangle = R_{2p}(r_1)R_{2p}(r_2)Y_{11}(\hat{\mathbf{r}}_1)Y_{11}(\hat{\mathbf{r}}_2)$$

Need to evaluate: $\left\langle 11,11\right|V_{ee}\left|11,11\right\rangle$

where $V_{ee} = \dfrac{e^2}{\left|\mathbf{r}_1-\mathbf{r}_2\right|} = e^2\sum_{\lambda\mu}\dfrac{4\pi}{2\lambda+1}\dfrac{r_<^\lambda}{r_>^{\lambda+1}}Y_{\lambda\mu}(\hat{\mathbf{r}}_1)Y^*_{\lambda\mu}(\hat{\mathbf{r}}_2)$

Define: $\mathcal{R}^\lambda(n_al_a,n_bl_b;n_cl_c,n_dl_d)$

$$=\int_0^\infty r_1^2dr_1\int_0^\infty r_2^2dr_2\,\frac{r_<^\lambda}{r_>^{\lambda+1}}R_{n_al_a}(r_1)R_{n_bl_b}(r_2)R_{n_cl_c}(r_1)R_{n_dl_d}(r_2)$$

$$\left\langle 11,11 \middle| V_{ee} \middle| 11,11 \right\rangle = e^2 \boldsymbol{\mathcal{R}}^0(2p,2p;2p,2p)G^2(1-1,00,11)$$

$$+e^2 \boldsymbol{\mathcal{R}}^2(2p,2p;2p,2p)\frac{G^2(1-1,20,11)}{5}$$

$$E(D) = e^2\left(\boldsymbol{\mathcal{R}}^0(2p,2p;2p,2p) + \frac{1}{25}\boldsymbol{\mathcal{R}}^2(2p,2p;2p,2p) \right)$$

Similarly, can show that:

$$E(P) = e^2\left(\boldsymbol{\mathcal{R}}^0(2p,2p;2p,2p) - \frac{5}{25}\boldsymbol{\mathcal{R}}^2(2p,2p;2p,2p) \right)$$

$$E(S) = e^2\left(\boldsymbol{\mathcal{R}}^0(2p,2p;2p,2p) + \frac{10}{25}\boldsymbol{\mathcal{R}}^2(2p,2p;2p,2p) \right)$$

Summary of results:

$$\mathscr{R}^{\lambda}(n_a l_a, n_b l_b; n_c l_c, n_d l_d)$$

$$= \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \, \frac{r_<^\lambda}{r_>^{\lambda+1}} R_{n_a l_a}(r_1) R_{n_b l_b}(r_2) R_{n_c l_c}(r_1) R_{n_d l_d}(r_2)$$

$$\mathscr{R}^{\lambda}(2p, 2p; 2p, 2p)$$

$$= \int_0^\infty r_1^2 dr_1 R_{2p}^2(r_1) \left(\int_0^{r_1} r_2^2 dr_2 \, \frac{r_2^\lambda}{r_1^{\lambda+1}} R_{2p}^2(r_2) + \int_{r_1}^\infty r_2^2 dr_2 \, \frac{r_1^\lambda}{r_2^{\lambda+1}} R_{2p}^2(r_2) \right)$$

$$E(P) = e^2\left(\mathcal{R}^0(2p,2p;2p,2p) - \frac{5}{25}\mathcal{R}^2(2p,2p;2p,2p) \right)$$

$$E(D) = e^2\left(\mathcal{R}^0(2p,2p;2p,2p) + \frac{1}{25}\mathcal{R}^2(2p,2p;2p,2p) \right)$$

$$E(S) = e^2\left(\mathcal{R}^0(2p,2p;2p,2p) + \frac{10}{25}\mathcal{R}^2(2p,2p;2p,2p) \right)$$

Taking into account anti-symmetry of two-particle wavefunction

More details of the total angular momentum $L = 2$ case:

$$\left|JM;l_1l_2\right\rangle = \left|22;11\right\rangle = \sum_{m_1,m_2}\left|l_1m_1,l_2m_2\right\rangle\left\langle l_1m_1,l_2m_2\right|JM;l_1l_2\rangle$$

$$= \left|11,11\right\rangle = R_{2p}(r_1)R_{2p}(r_2)Y_{11}(\hat{\mathbf{r}}_1)Y_{11}(\hat{\mathbf{r}}_2)$$

Note that $\psi_D(\mathbf{r}_1,\mathbf{r}_2) = \psi_D(\mathbf{r}_2,\mathbf{r}_1)$

Full wavefunction including spin

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\sigma_1,\sigma_2)=\psi_{L=2}(\mathbf{r}_1,\mathbf{r}_2)\chi(\sigma_1,\sigma_2)$$

Must be anti-symmetric

Summary of results for two spin-$\frac{1}{2}$ particle states:

$$\left|11;\tfrac{1}{2}\tfrac{1}{2}\right\rangle=\left|\tfrac{1}{2}\tfrac{1}{2},\tfrac{1}{2}\tfrac{1}{2}\right\rangle$$

$$\left|10;\tfrac{1}{2}\tfrac{1}{2}\right\rangle=\frac{1}{\sqrt{2}}\left(\left|\tfrac{1}{2}-\tfrac{1}{2},\tfrac{1}{2}\tfrac{1}{2}\right\rangle+\left|\tfrac{1}{2}\tfrac{1}{2},\tfrac{1}{2}-\tfrac{1}{2}\right\rangle\right)$$

$$\left|1-1;\tfrac{1}{2}\tfrac{1}{2}\right\rangle=\left|\tfrac{1}{2}-\tfrac{1}{2},\tfrac{1}{2}-\tfrac{1}{2}\right\rangle$$

S=1, symmetric
degeneracy:
2S+1=3

$$\left|00;\tfrac{1}{2}\tfrac{1}{2}\right\rangle=\frac{1}{\sqrt{2}}\left(\left|\tfrac{1}{2}-\tfrac{1}{2},\tfrac{1}{2}\tfrac{1}{2}\right\rangle-\left|\tfrac{1}{2}\tfrac{1}{2},\tfrac{1}{2}-\tfrac{1}{2}\right\rangle\right)$$

S=0,
anti-symmetric
degeneracy:
2S+1=1

Extending these arguments, Condon and Shortley concluded that in general *L+S=even*

→Valid atomic terms for Carbon:

$$^{(2S+1)}L_J$$

$$^3P = E_0 - 5e^2\mathcal{R}^2 / 25 = 0.00 \text{ eV}$$

$$^1D = E_0 + 1e^2\mathcal{R}^2 / 25 = 1.26 \text{ eV}$$

$$^1S = E_0 + 10e^2\mathcal{R}^2 / 25 = 2.68 \text{ eV}$$

$$\Rightarrow e^2\mathcal{R}^2 / 25 \sim 0.19 \text{ eV}$$

Summary of results for analysis of atomic term energies

$$\mathcal{H} = \underbrace{\sum_i h(\mathbf{r}_i)}_{\text{single electron terms}} + \sum_{i,j<i} \underbrace{\frac{e^2}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}}_{\text{electron-electron interaction}}$$

Evaluating expectation values: $\langle LM | \mathcal{H} | LM \rangle$ for $2p^2$

$$E(P) = e^2 \left(\mathcal{R}^0(2p,2p;2p,2p) - \frac{5}{25}\mathcal{R}^2(2p,2p;2p,2p) \right)$$

$$E(D) = e^2 \left(\mathcal{R}^0(2p,2p;2p,2p) + \frac{1}{25}\mathcal{R}^2(2p,2p;2p,2p) \right)$$

$$E(S) = e^2 \left(\mathcal{R}^0(2p,2p;2p,2p) + \frac{10}{25}\mathcal{R}^2(2p,2p;2p,2p) \right)$$

Another example – Ti^{+2} ($1s^2\ 2s^2\ 3s^2\ 2p^6\ 3p^6\ 3d^2$)

Note that for simplicity, the outer *4s²* electrons have been removed.

From NIST:

Configuration	Term	J	Level (eV)
$3p^6 3d^2$	^3F	2	0.0000
		3	0.02292
		4	0.05212
$3p^6 3d^2$	^1D	2	1.05058
$3p^6 3d^2$	^3P	0	1.30660
		1	1.31468
		2	1.32926
$3p^6 3d^2$	^1G	4	1.78507
$3p^6 3d^2$	^1S	0	4.02645

Condon & Shortley analysis:

$$^3F = E_0 - 8e^2\mathcal{R}^2/49 - 9e^2\mathcal{R}^4/441$$

$$^1D = E_0 - 3e^2\mathcal{R}^2/49 + 36e^2\mathcal{R}^4/441$$

$$^1G = E_0 + 4\mathcal{R}^2/49 + 1e^2\mathcal{R}^4/441$$

$$^3P = E_0 + 7e^2\mathcal{R}^2/49 - 84e^2\mathcal{R}^4/441$$

$$^1S = E_0 + 14e^2\mathcal{R}^2/49 + 126e^2\mathcal{R}^4/441$$

45 pairs of single particle states → 5 atomic terms