Multielectron atoms – going beyond independent electron approximation. The coupling of angular momenta

- **Independent electron approximation – IEA**
- **To each electron we may assign a quantum state, defined by a set of quantum numbers (n, l, m_l, m_s)**
- **The atom is characterized by a well defined electron configuration**
- **A configuration is defined by the number of electrons on each orbital (characterized by n and l)**

Ex: Phosphorus $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$.

- **The best IEA method is the Hartree-Fock method**
- **It takes into account the Pauli exclusion principle**
- **The totally antisymmetric wavefunctions are expressed by the Slater-determinants**

$$\phi(q_1, q_2, \ldots, q_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_\alpha(q_1) & u_\beta(q_1) & \cdots & u_\nu(q_1) \\ u_\alpha(q_2) & u_\beta(q_2) & \cdots & u_\nu(q_2) \\ \vdots & \vdots & & \vdots \\ u_\alpha(q_N) & u_\beta(q_N) & \cdots & u_\nu(q_N) \end{vmatrix}$$

- The Hartree-Fock method finds the best wavefunctions and energies within the IEA
- This is not exact because of the nonspherical components of the electron-electron interactions
- Part of these interactions are related to the coupling of angular momenta
  - Electrostatic interactions
  - Spin-orbit interactions
- We assume in the following calculation, that the electrostatic interactions are larger than the spin-orbit ones (Russel-Saunders coupling, valid for small Z atoms)

$\hat{\mathbf{L}}$ – the total orbital momentum of the electron system

$\hat{\mathbf{S}}$ – the total spin

$\hat{L}_z$ and $\hat{S}_z$ – the $0z$ components

- **These operators and H commute, so they have a common set of eigenfunctions**
- **These eigenfunctions should obey the eigenequations**

$$\begin{aligned} \hat{L}^2\phi &= L(L+1)\phi \\ \hat{L}_z\phi &= M_L\phi \\ \hat{S}^2\phi &= S(S+1)\phi \\ \hat{S}_z\phi &= M_S\phi. \end{aligned}$$

- **The Slater-determinants do not obey always these requirements**

- **The Slater-determinants are eigenfunctions of the one-electron angular momentum operators**

$$\begin{aligned}
\hat{l}_i^2\phi_1 &= l_i(l_i+1)\phi_1 \\
\hat{l}_{iz}\phi_1 &= m_{il}\phi_1 \\
\hat{s}_i^2\phi_1 &= s_i(s_i+1)\phi_1 \\
\hat{s}_{iz}\phi_1 &= m_{is}\phi_1,
\end{aligned}$$

where $i = \overline{1, N}$ and N being the number of electrons.

- **We want to construct wavefunctions from the Slater-determinants, which are eigenfunctions for the whole electron system.**
- **We make a transformation from the one-electron angular momenta representation to the total angular momentum representation**
- **This procedure is the coupling of angular momenta**

- System with 2 electrons
- At this moment we neglect the spin
- The relationship between the one-electron (l_1,m_1,l_2,m_2) and the total angualar momentum (l_1,l_2,L,M) representation may be written

$$|l_1 l_2 L M_L\rangle = \sum_{m_{l1} m_{l2}} |l_1 m_{l1} l_2 m_{l2}\rangle\langle l_1 m_{l1} l_2 m_{l2}|l_1 l_2 L M_L\rangle$$

$$= \sum_{m_{l1} m_{l2}} C^{L M_L}_{l_1 m_{l1} l_2 m_{l2}} |l_1 m_{l1} l_2 m_{l2}\rangle.$$

Here we have used that the sum of the projectors $|l_1 m_{l1} l_2 m_{l2}\rangle\langle l_1 m_{l1} l_2 m_{l2}|$ for every possible m_{l1} and m_{l2} magnetic quantum numbers with $m_{l1} + m_{l2} = M_L$ projects to the subspace generated by the $|l_1 l_2 L M_L\rangle$ vector, so it does not change this vector. The occurring overlap integrals are the $C^{L M_L}_{l_1 m_{l1} l_2 m_{l2}}$ Clebsch–Gordan coefficients.

- **Taking into account the spins**

$$|l_1 l_2 L S M_L M_S\rangle = \sum_{m_{l1} m_{l2}} \sum_{m_{s1} m_{s2}} C^{L M_L}_{l_1 m_{l1} l_2 m_{l2}} C^{S M_S}_{s_1 m_{s1} s_2 m_{s2}} \times |l_1 m_{l1} l_2 m_{l2} s_1 m_{s1} s_2 m_{s2}\rangle,$$

where $s_1 = s_2 = 1/2$.

Electrostatic corrections to the Hartree-Fock method

- Orbit-orbit and spin-spin interactions
- Russel-Saunders coupling
- We neglect the spin-orbit interactions
- Perturbational method
- The unperturbed wavefunctions are eigenfunctions of $\mathbf{L}^2,\ \mathbf{S}^2,\ L_z \text{ and } S_z$
- The first-order perturbational correction may be written

$$E_k^{(1)} = \langle k l_1 l_2 \cdots l_N L S M_L M_S | H' | k l_1 l_2 \cdots l_N L S M_L M_S \rangle$$

- The vector $|kl_1l_2\cdots l_N LSM_LM_S\rangle$ may be expressed as a linear combination of Slater determinants

- Example for the dependence of the energy on the spin coupling – the helium atom
- Triplet case – S=1, orthohelium

$$|0l_2L1M_LM_S\rangle = \sum_{m_{s1}m_{s2}} C^{1M_S}_{\frac{1}{2}m_{s1}\frac{1}{2}m_{s2}} |00l_2m_{l2}\tfrac{1}{2}m_{s1}\tfrac{1}{2}m_{s2}\rangle$$

$$l_1 = m_{l1} = 0 \qquad l_2 = L \equiv l,\ m_{l2} = M_L \equiv m$$

$$M_S = \pm 1$$

$$\begin{aligned} |0ll1m_{l2} \pm 1\rangle &= C^{1\pm1}_{\frac{1}{2}\pm\frac{1}{2}\,\frac{1}{2}\pm\frac{1}{2}} |00lm\tfrac{1}{2} \pm \tfrac{1}{2}\tfrac{1}{2} \pm \tfrac{1}{2}\rangle \\ &= |00lm\tfrac{1}{2} \pm \tfrac{1}{2}\tfrac{1}{2} \pm \tfrac{1}{2}\rangle. \end{aligned}$$

- **The sum reduces to one term -> one Slater-determinant**
- **Separating the spatial and the spin part of the wavefunction**

$$\begin{aligned} \Psi_{1\pm1}(q_1, q_2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{100}(r_1)\chi_{\pm\frac{1}{2}}(1) & \psi_{nlm}(\mathbf{r_1})\chi_{\pm\frac{1}{2}}(1) \\ \psi_{100}(r_2)\chi_{\pm\frac{1}{2}}(2) & \psi_{nlm}(\mathbf{r_2})\chi_{\pm\frac{1}{2}}(2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}}[\psi_{100}(r_1)\psi_{nlm}(\mathbf{r_2}) - \psi_{nlm}(\mathbf{r_1})\psi_{100}(r_2)] \\ &\quad \times \chi_{\pm\frac{1}{2}}(1)\chi_{\pm\frac{1}{2}}(2). \end{aligned}$$

$M_S = 0$

$$
\begin{aligned}
|0ll1m0\rangle &= C^{10}_{\frac{1}{2},\frac{1}{2},\frac{1}{2},-\frac{1}{2}} |00lm\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\text{-}\tfrac{1}{2}\rangle \\
&\quad + C^{10}_{\frac{1}{2},-\frac{1}{2},\frac{1}{2},\frac{1}{2}} |00lm\tfrac{1}{2}\text{-}\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\rangle \\
&= \frac{1}{\sqrt{2}} \left[|00lm\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\text{-}\tfrac{1}{2}\rangle + |00lm\tfrac{1}{2}\ \text{-}\tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\rangle \right]
\end{aligned}
$$

- **The Slater-determinants**

$$
\begin{aligned}
\Psi_{10}(q_1,q_2) &= \frac{1}{2}\left[\begin{vmatrix} \psi_{100}(r_1)\chi_{+\frac{1}{2}}(1) & \psi_{nlm}(\mathbf{r_1})\chi_{-\frac{1}{2}}(1) \\ \psi_{100}(r_2)\chi_{+\frac{1}{2}}(2) & \psi_{nlm}(\mathbf{r_2})\chi_{-\frac{1}{2}}(2) \end{vmatrix}\right. \\
&\left. + \begin{vmatrix} \psi_{100}(r_1)\chi_{-\frac{1}{2}}(1) & \psi_{nlm}(\mathbf{r_1})\chi_{+\frac{1}{2}}(1) \\ \psi_{100}(r_2)\chi_{-\frac{1}{2}}(2) & \psi_{nlm}(\mathbf{r_2})\chi_{+\frac{1}{2}}(2) \end{vmatrix}\right] \\
&= \frac{1}{\sqrt{2}}[\psi_{100}(r_1)\psi_{nlm}(\mathbf{r_2}) - \psi_{nlm}(\mathbf{r_1})\psi_{100}(r_2)] \\
&\times \frac{1}{\sqrt{2}}[\chi_{+\frac{1}{2}}(1)\chi_{-\frac{1}{2}}(2) + \chi_{-\frac{1}{2}}(1)\chi_{+\frac{1}{2}}(2)].
\end{aligned}
$$

- **Singlet case – S=0, parahelium**

$$
\begin{aligned}
|0ll1m00\rangle &= \sum_{m_{s1}m_{s2}} C^{00}_{\frac{1}{2}m_{s1}\frac{1}{2}m_{s2}} |00lm\tfrac{1}{2}m_{s1}\tfrac{1}{2}m_{s2}\rangle \\
&= C^{00}_{\frac{1}{2},\frac{1}{2},\frac{1}{2},-\frac{1}{2}} |00lm\tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\ \text{-}\tfrac{1}{2}\rangle \\
&\quad + C^{00}_{\frac{1}{2},-\frac{1}{2},\frac{1}{2},\frac{1}{2}} |00lm\tfrac{1}{2}\ \text{-}\tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\rangle \\
&= \frac{1}{\sqrt{2}} \left[|00lm\tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\ \text{-}\tfrac{1}{2}\rangle - |00lm\tfrac{1}{2}\ \text{-}\tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\rangle \right]
\end{aligned}
$$

- **The Slater-determinants**

$$
\begin{aligned}
\Psi_{00}(q_1,q_2) &= \frac{1}{2}\left[\begin{vmatrix} \psi_{100}(r_1)\chi_{+\frac{1}{2}}(1) & \psi_{nlm}(\mathbf{r_1})\chi_{-\frac{1}{2}}(1) \\ \psi_{100}(r_2)\chi_{+\frac{1}{2}}(2) & \psi_{nlm}(\mathbf{r_2})\chi_{-\frac{1}{2}}(2) \end{vmatrix}\right. \\
&\quad \left. - \begin{vmatrix} \psi_{100}(r_1)\chi_{-\frac{1}{2}}(1) & \psi_{nlm}(\mathbf{r_1})\chi_{+\frac{1}{2}}(1) \\ \psi_{100}(r_2)\chi_{-\frac{1}{2}}(2) & \psi_{nlm}(\mathbf{r_2})\chi_{+\frac{1}{2}}(2) \end{vmatrix}\right] \\
&= \frac{1}{\sqrt{2}}[\psi_{100}(r_1)\psi_{nlm}(\mathbf{r_2}) + \psi_{nlm}(\mathbf{r_1})\psi_{100}(r_2)] \\
&\quad \times \frac{1}{\sqrt{2}}[\chi_{+\frac{1}{2}}(1)\chi_{-\frac{1}{2}}(2) - \chi_{-\frac{1}{2}}(1)\chi_{+\frac{1}{2}}(2)]
\end{aligned}
$$

The $\langle \Psi_{SM_S} | H' | \Psi_{SM_S} \rangle$ correction will depend on S.

- **The spatial wavefunction**

$$\Psi_k^+(\mathbf{r_1}, \mathbf{r_2}) = \frac{1}{\sqrt{2}}[\psi_a(\mathbf{r_1})\psi_b(\mathbf{r_2}) + \psi_b(\mathbf{r_1})\psi_a(\mathbf{r_2})]; \quad S = 0$$

$$\Psi_k^-(\mathbf{r_1}, \mathbf{r_2}) = \frac{1}{\sqrt{2}}[\psi_a(\mathbf{r_1})\psi_b(\mathbf{r_2}) - \psi_b(\mathbf{r_1})\psi_a(\mathbf{r_2})]; \quad S = 1,$$

$$E^0_{n_a n_b} = -\frac{Z^2}{2}\left(\frac{1}{n_a^2} + \frac{1}{n_b^2}\right).$$

$n_a = 1$, $n_b \equiv n$

$$E_n^0 = -\frac{Z^2}{2}\left(1 + \frac{1}{n^2}\right). \tag{28}$$

$2n^2$ times degenerated unperturbed states
$H' = 1/r_{12}$

$$\det(\langle \Psi^{\pm}_{nlm} | H' | \Psi^{\pm}_{nl'm'} \rangle - \delta_{ll'}\delta_{mm'}\delta_{\pm\pm}E_n^{(1)}) = 0. \tag{29}$$

All nondiagonal elements will be zero

$$\begin{aligned}
\langle \Psi^{+}_{nlm} | \frac{1}{r_{12}} | \Psi^{-}_{nl'm'} \rangle \quad &= \\
= \frac{1}{2}[&\langle \psi_{100}\psi_{nlm} | \frac{1}{r_{12}} | \psi_{100}\psi_{nl'm'} \rangle + \langle \psi_{nlm}\psi_{100} | \frac{1}{r_{12}} | \psi_{100}\psi_{nl'm'} \rangle \\
&- \langle \psi_{100}\psi_{nlm} | \frac{1}{r_{12}} | \psi_{nl'm'}\psi_{100} \rangle - \langle \psi_{nlm}\psi_{100} | \frac{1}{r_{12}} | \psi_{nl'm'}\psi_{100} \rangle] \\
= \quad &0,
\end{aligned} \tag{30}$$

and

$$\begin{aligned}
\langle \Psi^{\pm}_{nlm} | \frac{1}{r_{12}} | \Psi^{\pm}_{nl'm'} \rangle \quad = \quad &\langle \psi_{100}\psi_{nlm} | \frac{1}{r_{12}} | \psi_{100}\psi_{nl'm'} \rangle \\
&\pm \langle \psi_{100}\psi_{nlm} | \frac{1}{r_{12}} | \psi_{nl'm'}\psi_{100} \rangle,
\end{aligned} \tag{31}$$

different from 0 only, if $l = l'$ and $m = m'$

The corrections are obtained by the diagonal elements

$$\begin{aligned} E^{(1)}_{nl\pm} &= \langle \Psi^{\pm}_{nlm} | H' | \Psi^{\pm}_{nl'm'} \rangle \\ &= \langle \psi_{100}\psi_{nlm} | \frac{1}{r_{12}} | \psi_{100}\psi_{nlm} \rangle \\ &\quad \pm \langle \psi_{nlm}\psi_{100} | \frac{1}{r_{12}} | \psi_{nlm}\psi_{100} \rangle \\ &= J_{nl} \pm K_{nl}. \end{aligned} \tag{32}$$

J_{nl} Coulomb term

K_{nl} exchange term

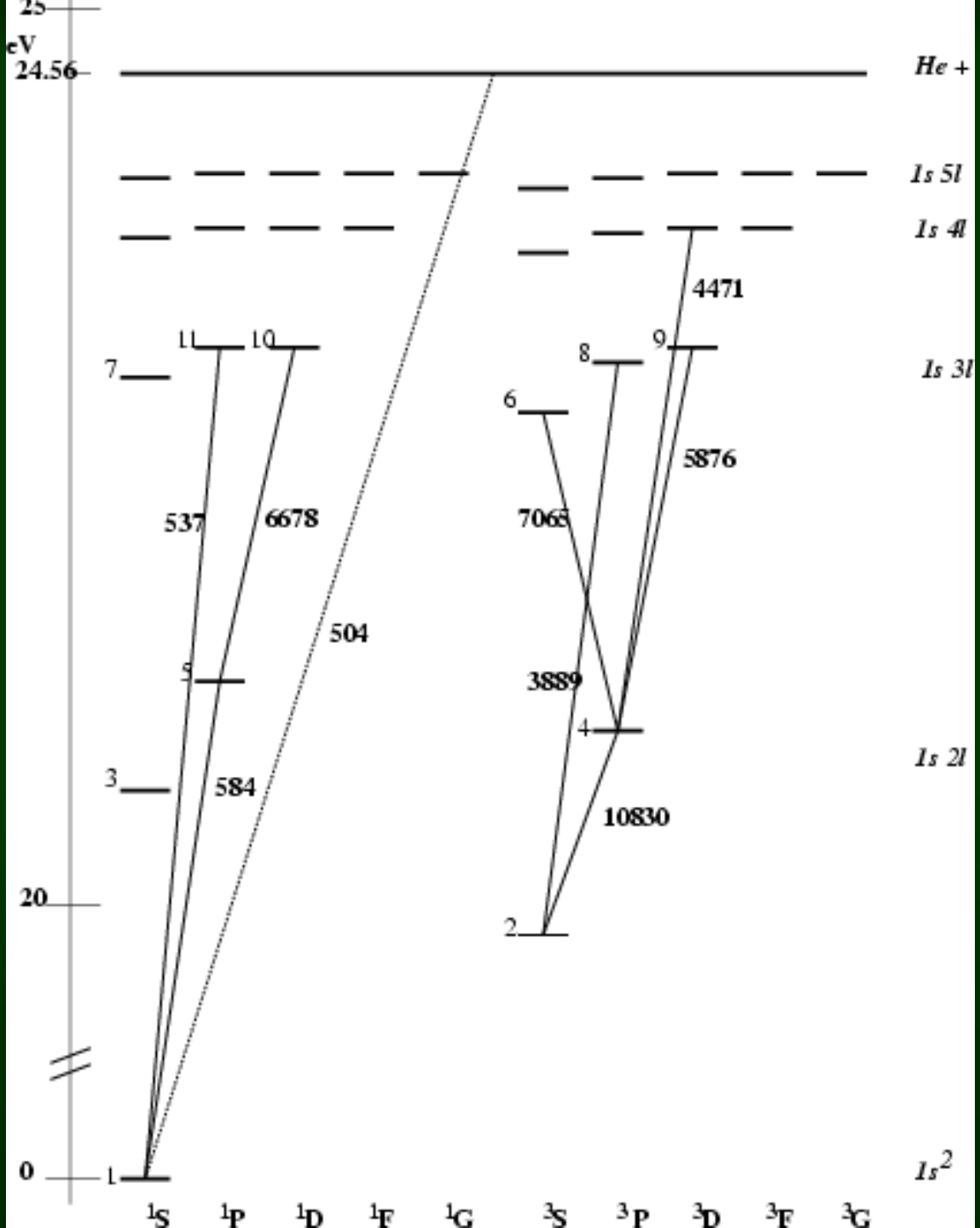
$$J_{nl} = \int_0^\infty dr_2 r_2^2 R_{nl}^2(r_2) \int_0^\infty dr_1 r_1^2 R_{10}^2(r_1) \frac{1}{r_>} \tag{33}$$

$$\begin{aligned} K_{nl} &= \frac{1}{2l+1} \int_0^\infty dr_2 r_2^2 R_{10}(r_2) R_{nl}(r_2) \\ &\quad \times \int_0^\infty dr_1 r_1^2 R_{10}(r_1) \frac{r_<^l}{r_>^{l+1}} R_{nl}(r_1), \end{aligned} \tag{34}$$

Finally

$$E_{nl\pm} = -\frac{Z^2}{2}\left(1 + \frac{1}{n^2}\right) + J_{nl} \pm K_{nl} \tag{35}$$

The enrgy of the ortho (triplet) state will be lower than the enrgy of the para (singlet) state


25
eV
24.56
He +
1s 5l
1s 4l
4471
11
10
9
8
7
6
1s 3l
5876
537
6678
7065
504
5
3889
4
3
584
1s 2l
10830
20
2
0
1
1s2
1S
1P
1D
1F
1G
3S
3P
3D
3F
3G

- **More general – Hund's rule for the spin:**

  For a given electron configuration, the term with maximum multiplicity (2S+1) has the lowest energy.

- **Hund's rule for the angular momentum**

  For a given multiplicity, the term with the largest value of L has the lowest energy.

We give an example also for the dependence of the energy on L. Let's consider an atom with two p electrons on its outer shell. If these are equivalent (has the same principal and orbital quantum numbers), the possible terms are ${}^1S$, ${}^1D$ and ${}^3P$. Taking into account the previous discussions, the triplet state will have the lowest energy. We will compare the energy of the two singlet terms, in order to investigate the L-dependence

We may take only the spatial part of the wavefunctions

$$|11LM_L\rangle = \sum_{m_{l1},m_{l2}} C^{LM_L}_{1m_{l1}1m_{l2}} |1m_{l1}1m_{l2}\rangle. \tag{37}$$

If $L = 0$

$$|1100\rangle = \frac{1}{\sqrt{3}} \left[|111\text{-}1\rangle - |1010\rangle + |1\text{-}111\rangle \right]. \tag{38}$$

In the H' perturbational potential only the term containing the interaction of the two electrons $1/r_{12}$ will depend on L.

$$\begin{aligned} \langle 1100| \frac{1}{r_{12}} |1100\rangle \quad = \quad & \frac{1}{3} \left[2\langle 111\text{-}1| \frac{1}{r_{12}} |111\text{-}1\rangle + \langle 1010| \frac{1}{r_{12}} |1010\rangle \right. \\ & \left. +2\langle 111\text{-}1| \frac{1}{r_{12}} |1\text{-}111\rangle - 4\langle 1010| \frac{1}{r_{12}} |111\text{-}1\rangle \right]. \end{aligned} \tag{39}$$

The matrix elements can be calculated with the known method. For the first two terms from the expansion of $1/r_{12}$ remain only $l = 0,\ 2$, $m_l = 0$ for the third term $l = 2$, $m_l = 2$, while for the last one $l = 2$, $m_l = 1$. Performing the calculations we get

$$\begin{aligned}\langle 1100|\frac{1}{r_{12}}|1100\rangle &= \int_0^\infty dr_1 r_1^2 R_p(r_1)^2 \int_0^\infty dr_2 r_2^2 R_p(r_2)\frac{1}{r_>} \\ &+ \frac{2}{5}\int_0^\infty dr_1 r_1^2 R_p(r_1)^2 \int_0^\infty dr_2 r_2^2 R_p(r_2)\frac{r_<^2}{r_>^3}. \qquad (40)\end{aligned}$$

If $L = 2$, the form of the (37) expansion depends on the value of M_L. But the energy without any external field cannot depend on M_L, and we can choose a value, for example $M_L = 2$

$$|l_1 = 1, l_2 = 1, L = 2, M_L = 2\rangle = |l_1 = 1, m_{l1} = 1, l_2 = 1, m_{l2} = 1\rangle, \qquad (41)$$

and the matrix element of $1/r_{12}$ will be

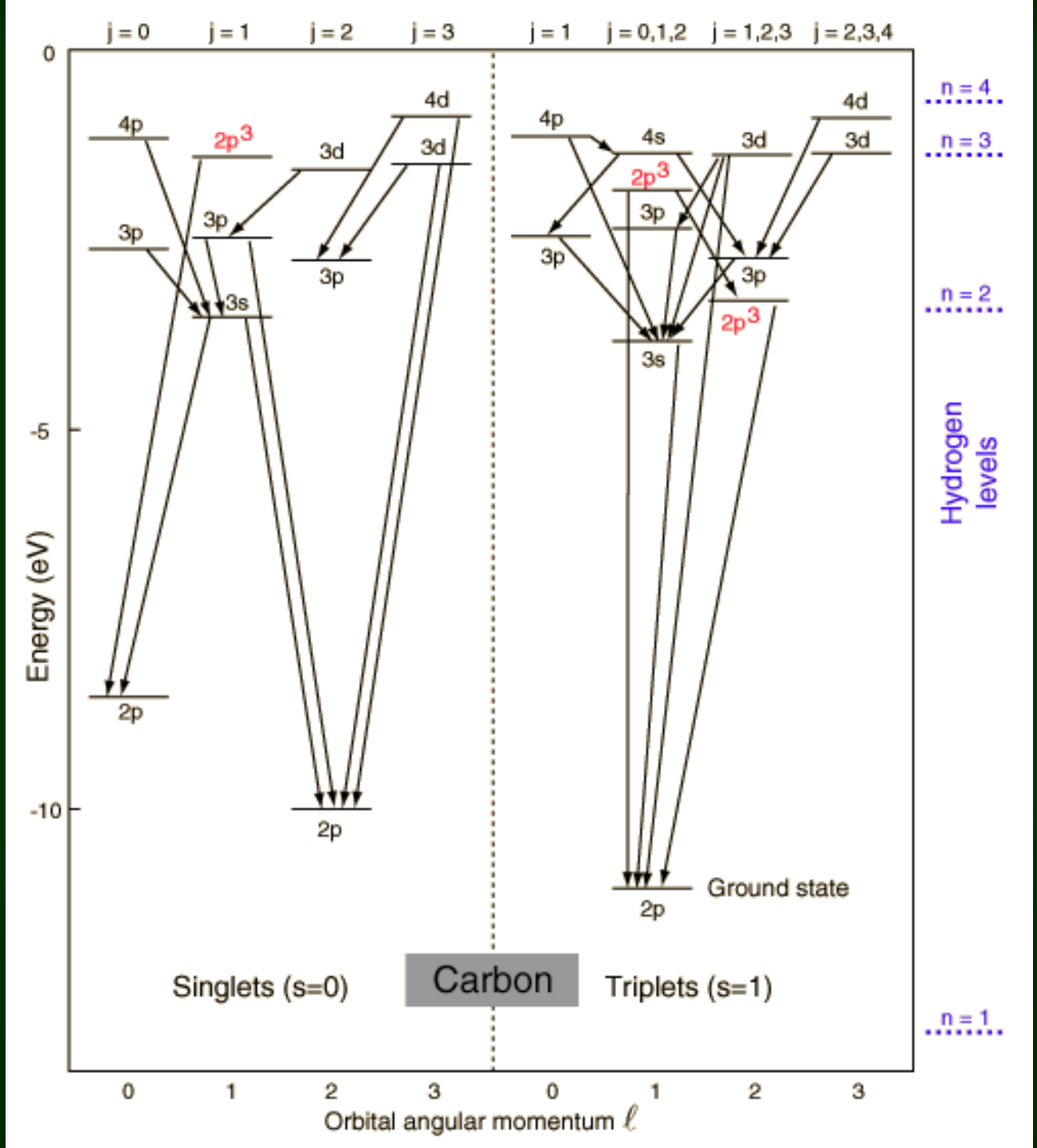
$$\langle l_1 = 1, l_2 = 1, L = 2, M_L = 2|\frac{1}{r_{12}}|l_1 = 1, l_2 = 1, L = 2, M_L = 2\rangle \quad =$$

$$= \langle l_1 = 1, m_{l1} = 1, l_2 = 1, m_{l2} = 1|\frac{1}{r_{12}}|l_1 = 1, m_{l1} = 1, l_2 = 1, m_{l2} = 1\rangle$$

$$= \int_0^\infty dr_1 r_1^2 R_p(r_1)^2 \int_0^\infty dr_2 r_2^2 R_p(r_2)\frac{1}{r_>}$$

$$+\frac{1}{25}\int_0^\infty dr_1 r_1^2 R_p(r_1)^2 \int_0^\infty dr_2 r_2^2 R_p(r_2)\frac{r_<^2}{r_>^3} \qquad (42)$$

All radial integrals are positive, so the energy of the $L = 2$ state will be lower than that with $L = 0$ because $1/25 < 2/5$.


j = 0
j = 1
j = 2
j = 3
j = 1
j = 0,1,2
j = 1,2,3
j = 2,3,4
0
-5
-10
Energy (eV)
4p
2p3
3d
4d
3d
3p
3p
3s
2p
3p
2p
4p
4s
3d
4d
3d
2p3
3p
3p
3p
2p3
3s
2p
Ground state
n = 4
n = 3
n = 2
n = 1
Hydrogen levels
Singlets (s=0)
Carbon
Triplets (s=1)
0
1
2
3
0
1
2
3
Orbital angular momentum ℓ