Teoria quantistica Sistemi semplici risolvibili esattamente

ATOMO DI IDROGENO

Transizioni spettroscopiche

Regole di selezione

Orbitali atomici s,p,d

Chimica Fisica 2

Laurea Tri. Chim. In. 2022-23

Lun 8-5-2023

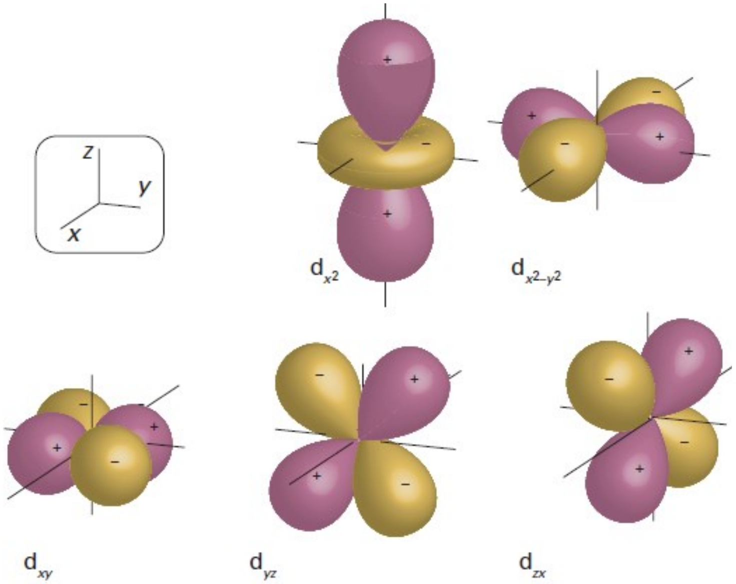
Prof. Antonio Toffoletti

Atomic structure

9.2 Atomic orbitals and their energies

(h) d Orbitals

When $n = 3$, l can be 0, 1, or 2. As a result, this shell consists of one 3s orbital, three 3p orbitals, and five 3d orbitals. Each value of the quantum number $m_l = +2, +1, 0, -1, -2$ corresponds to a different value for the component of the angular momentum about the z-axis. As for the p orbitals, d orbitals with opposite values of m_l (and hence opposite senses of motion around the z-axis) may be combined in pairs to give real standing waves, and the boundary surfaces of the resulting shapes are shown in Fig. 9.16. The real linear combinations have the following forms:



$$d_{xy} = xyf(r) \qquad d_{yz} = yzf(r) \qquad d_{zx} = zxf(r)$$

$$d_{x^2-y^2} = \tfrac{1}{2}(x^2 - y^2)f(r) \qquad d_{z^2} = (\tfrac{1}{2}\sqrt{3})(3z^2 - r^2)f(r)$$

Atomic structure

9.3 Spectroscopic transitions and selection rules

Le energie degli atomi idrogenoidi sono date dalla seguente equazione:

$$E_n = -\frac{Z^2 \mu e^4}{32\pi^2 \varepsilon_0^2 \hbar^2 n^2}$$

Quando l'elettrone subisce una transizione, un cambiamento di stato, da un orbitale con numeri quantici n_1, l_1, m_{l1} ad un altro orbitale di energia inferiore con numeri quantici n_2, l_2, m_{l2}, subisce un cambiamento di energia ΔE ed elimna l'energia in eccesso sotto forma di un fotone di radiazione elettro-magnetica con frequenza ν data dalla condizione sulla frequenza di Bohr $\Delta E = h\nu$.

Si potrebbe pensare che tutte le possibili transizioni siano consentite e che lo spettro di emissione nasca dalla transizione di un elettrone da qualsiasi orbitale iniziale a qualsiasi altro orbitale. Tuttavia non è così, perché un fotone ha un momento angolare di spin intrinseco corrispondente a s = 1. Poiché il momento angolare totale si conserva, la variazione del momento angolare dell'elettrone deve compensare il momento angolare portato via dal fotone.

Atomic structure

9.3 Spectroscopic transitions and selection rules

Quindi, un elettrone in un orbitale ***d*** (l = 2) non può effettuare una transizione verso un orbitale ***s*** (l = 0) perché il fotone non può portare via abbastanza momento angolare. Allo stesso modo, un elettrone ***s*** non può effettuare una transizione verso un'altro orbitale ***s***, perché non ci sarebbe alcun cambiamento nel momento angolare dell'elettrone per compensare il momento angolare portato via dal fotone. Ne consegue che alcune transizioni spettroscopiche sono ***PERMESSE***, il che significa che possono verificarsi, mentre altre sono ***PROIBITE***, nel senso che non possono verificarsi.

Una regola di selezione è una affermazione su quali transizioni sono ***PERMESSE***. Per gli atomi vengono derivate identificando le transizioni che conservano il momento angolare quando un fotone viene emesso o assorbito. Le regole di selezione per gli atomi idrogenoidi sono

$$\Delta l = \pm 1 \qquad \Delta m_l = 0, \pm 1$$

The principal quantum number n can change by any amount consistent with the Δl
for the transition, because it does not relate directly to the angular momentum.

Atomic structure

9.3 Spectroscopic transitions and selection rules

COME TROVARE LE REGOLE DI SELEZIONE - 1

The underlying classical idea behind a spectroscopic transition is that, for an atom or molecule to be able to interact with the electromagnetic field and absorb or create a photon of frequency ν, it must possess, at least transiently, a dipole oscillating at that frequency. This transient dipole is expressed quantum mechanically in terms of the **transition dipole moment, $\boldsymbol{\mu}_{\mathrm{fi}}$**, between the initial and final states, where[1]

$$\boldsymbol{\mu}_{\mathrm{fi}} = \int \psi_{\mathrm{f}}^{*}\hat{\boldsymbol{\mu}}\psi_{\mathrm{i}}\,\mathrm{d}\tau \qquad (9.25)$$

and $\hat{\boldsymbol{\mu}}$ is the electric dipole moment operator. For a one-electron atom $\hat{\boldsymbol{\mu}}$ is multiplication by $-e\boldsymbol{r}$ with components $\mu_x = -ex$, $\mu_y = -ey$, and $\mu_z = -ez$. If the transition dipole moment is zero, then the transition is forbidden; the transition is allowed if the transition moment is nonzero.

$$\Delta l = \pm 1 \qquad \Delta m_l = 0, \pm 1$$

Atomic structure

9.3 Spectroscopic transitions and selection rules

COME TROVARE LE REGOLE DI SELEZIONE - 2

To evaluate a transition dipole moment, we consider each component in turn. For example, for the z-component,

$$\mu_{z,\mathrm{fi}} = -e\int \psi_\mathrm{f}^* z \psi_\mathrm{i}\,\mathrm{d}\tau$$

To evaluate the integral, we note from Table 8.2 that $z = (4\pi/3)^{1/2} r Y_{1,0}$, so

$$\int \psi_\mathrm{f}^* z \psi_\mathrm{i}\,\mathrm{d}\tau = \int_0^\infty\int_0^\pi\int_0^{2\pi} \overbrace{R_{n_\mathrm{f},l_\mathrm{f}} Y_{l_\mathrm{f},m_{l,\mathrm{f}}}^*}^{\psi_\mathrm{f}^*} \overbrace{\left(\frac{4\pi}{3}\right)^{1/2} r Y_{1,0}}^{z} \overbrace{R_{n_\mathrm{i},l_\mathrm{i}} Y_{l_\mathrm{i},m_{l,\mathrm{i}}}}^{\psi_\mathrm{i}} \overbrace{r^2\mathrm{d}r \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi}^{\mathrm{d}\tau}$$

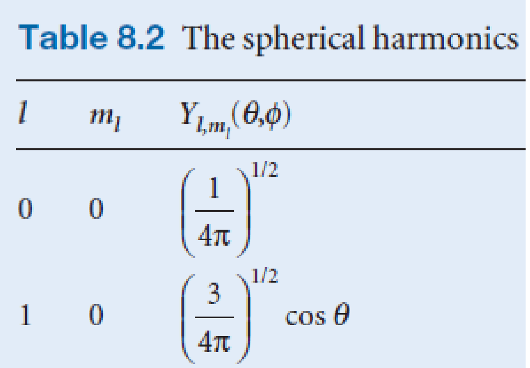


Table 8.2 The spherical harmonics

l	m_l	$Y_{l,m_l}(\theta,\phi)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$

This multiple integral is the product of three factors, an integral over r and two integrals over the angles, so the factors on the right can be grouped as follows:

$$\int \psi_\mathrm{f}^* z \psi_\mathrm{i}\,\mathrm{d}\tau = \left(\frac{4\pi}{3}\right)^{1/2}\int_0^\infty R_{n_\mathrm{f},l_\mathrm{f}} r R_{n_\mathrm{i},l_\mathrm{i}} r^2\mathrm{d}r \int_0^\pi\int_0^{2\pi} Y_{l_\mathrm{f},m_{l,\mathrm{f}}}^* Y_{1,0} Y_{l,m_{l,\mathrm{i}}} \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$

It follows from the properties of the spherical harmonics (Table 8.2) that the integral

$$\int_0^\pi\int_0^{2\pi} Y_{l_\mathrm{f},m_{l,\mathrm{f}}}^* Y_{1,m} Y_{l_\mathrm{i},m_{l,\mathrm{i}}} \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$

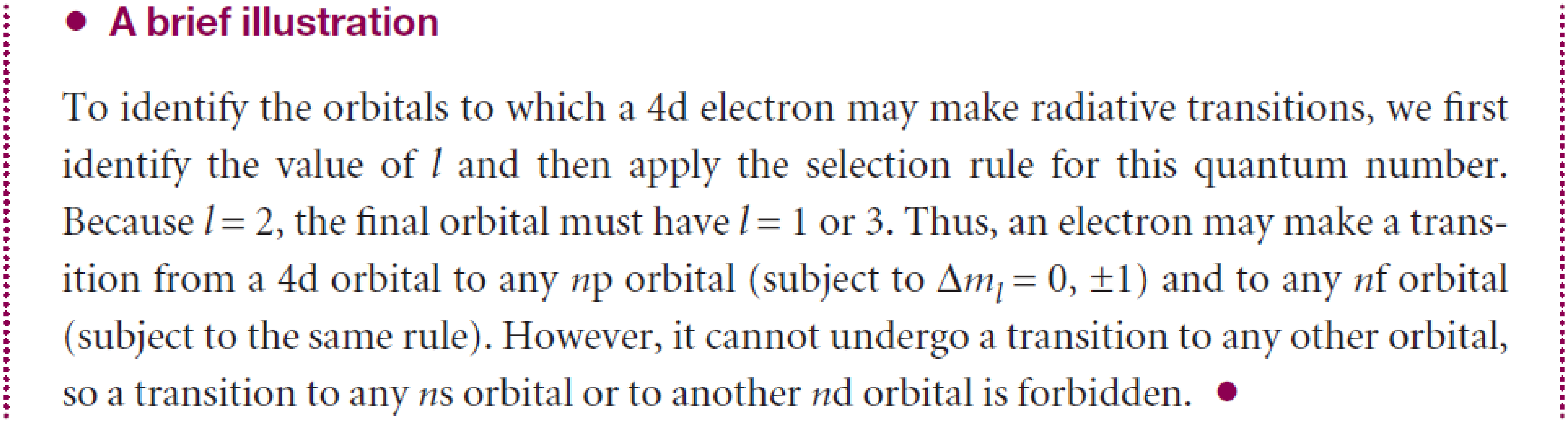
is zero unless $l_\mathrm{f} = l_\mathrm{i} \pm 1$ and $m_{l,\mathrm{f}} = m_{l,\mathrm{i}} + m$. Because $m = 0$ in the present case, the angular integral, and hence the z-component of the transition dipole moment, is zero unless $\Delta l = \pm 1$ and $\Delta m_l = 0$, which is a part of the set of selection rules. The same procedure, but considering the x- and y-components, results in the complete set of rules.

Atomic structure

9.3 Spectroscopic transitions and selection rules

COME TROVARE LE REGOLE DI SELEZIONE - 3

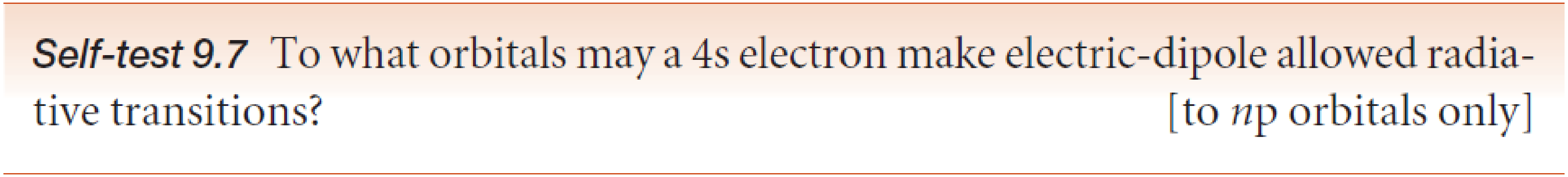
ESERCIZIO 1



- **A brief illustration**

To identify the orbitals to which a 4d electron may make radiative transitions, we first identify the value of l and then apply the selection rule for this quantum number. Because $l = 2$, the final orbital must have $l = 1$ or 3. Thus, an electron may make a transition from a 4d orbital to any np orbital (subject to $\Delta m_l = 0, \pm 1$) and to any nf orbital (subject to the same rule). However, it cannot undergo a transition to any other orbital, so a transition to any ns orbital or to another nd orbital is forbidden. ●

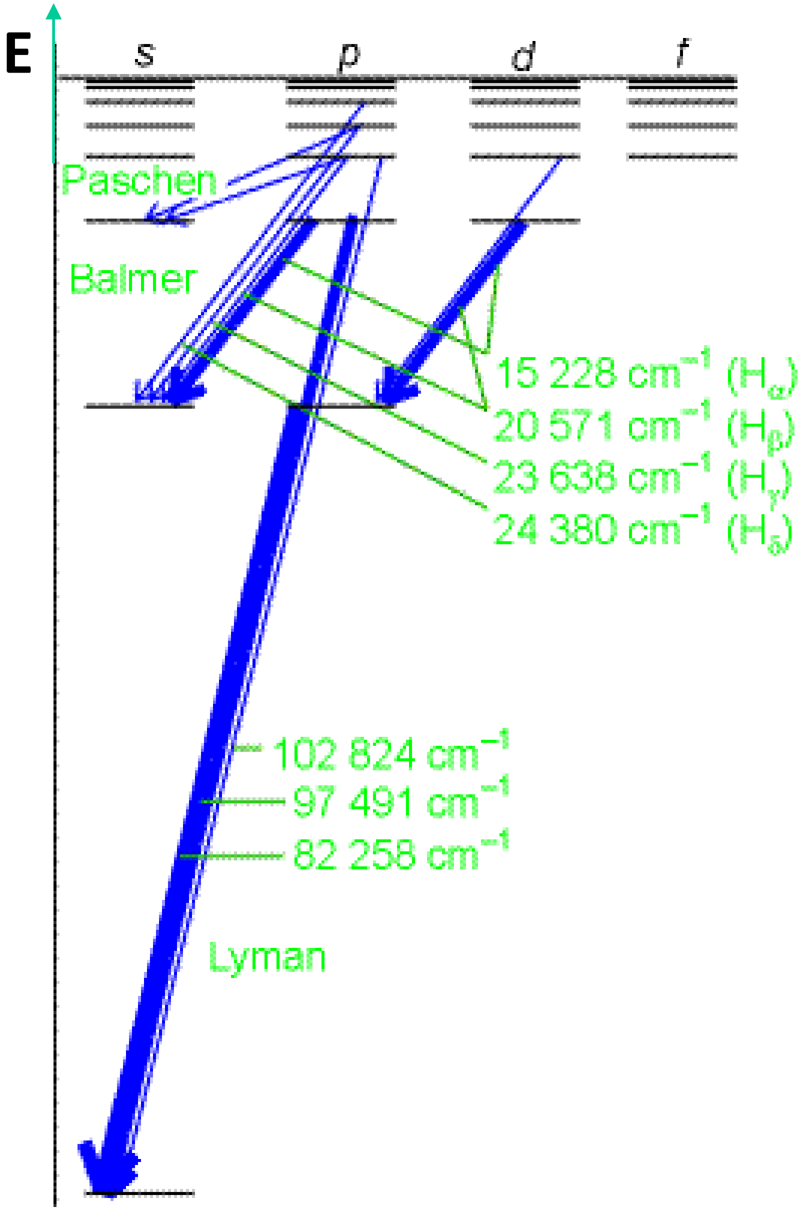
ESERCIZIO 2



Self-test 9.7 To what orbitals may a 4s electron make electric-dipole allowed radiative transitions? [to np orbitals only]

Atomic structure

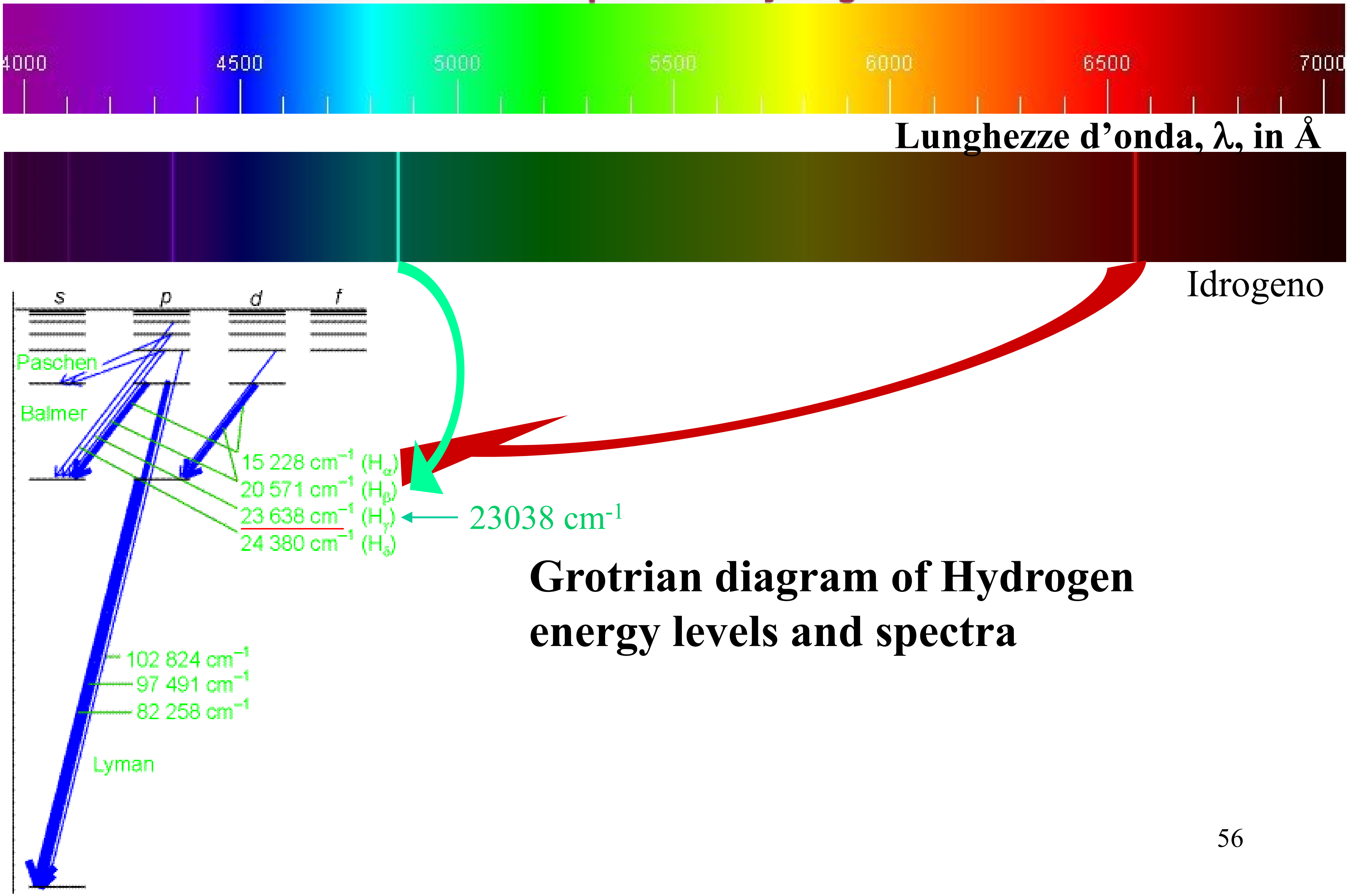
9.3 Spectroscopic transitions and selection rules



Le regole di selezione e i livelli di energia atomica insieme spiegano congiuntamentela struttura di un diagramma di Grotrian (Vedi Figura), che riassume le **energie degli stati** e le **transizioni tra di loro**. Gli spessori delle linee di transizione nel diagramma denotano le loro intensità relative nello spettro; vediamo come determinare la transizione intensità nella sezione 13.2.

Atomic structure

The structure and spectra of hydrogenic atoms



Grotrian diagram of Hydrogen energy levels and spectra

Atomic structure

The structures of many-electron atoms

9.4 The orbital approximation

Key points In the orbital approximation, each electron is regarded as occupying its own orbital. (a) A configuration is a statement of the occupied orbitals. (b) The Pauli exclusion principle, a special case of the Pauli principle, limits to two the number of electrons that can occupy a given orbital. (c) In many-electron atoms, s orbitals lie at a lower energy than p orbitals of the same shell due to the combined effects of penetration and shielding. (d) The building-up principle is an algorithm for predicting the ground-state electron configuration of an atom. (e) Ionization energies and electron affinities vary periodically through the periodic table.

The wavefunction of a many-electron atom is a very complicated function of the coordinates of all the electrons, and we should write it $\Psi(r_1,r_2,\ldots)$, where r_i is the vector from the nucleus to electron i (upper-case Ψ is commonly used to denote a many-electron wavefunction). However, in the **orbital approximation** we suppose that a reasonable first approximation to this exact wavefunction is obtained by thinking of each electron as occupying its 'own' orbital, and write

$$\Psi(r_1,r_2,\ldots) = \psi(r_1)\psi(r_2)\ldots \qquad (9.26)$$

Orbital approximation

We can think of the individual orbitals as resembling the hydrogenic orbitals, but corresponding to nuclear charges modified by the presence of all the other electrons in the atom. This description is only approximate, as the following *Justification* reveals, but it is a useful model for discussing the chemical properties of atoms, and is the starting point for more sophisticated descriptions of atomic structure.

Atomic structure

The structures of many-electron atoms

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Atomic structure

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$$\Psi(r_1, r_2, \ldots)$$

APPROSSIMAZIONE
ORBITALICA

$$\Psi(r_1, r_2, \ldots) = \psi(r_1)\psi(r_2)\ldots$$

Atomic structure

The structures of many-electron atoms

……

Justification 9.5 *The orbital approximation*

The orbital approximation would be exact if there were no interactions between electrons. To demonstrate the validity of this remark, we need to consider a system in which the hamiltonian for the energy is the sum of two contributions, one for electron 1 and the other for electron 2:

$$\hat{H} = \hat{H}_1 + \hat{H}_2$$

In an actual atom (such as helium atom), there is an additional term (proportional to $1/r_{12}$) corresponding to the interaction of the two electrons:

$$\hat{H} = \overbrace{-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{e^2}{4\pi\varepsilon_0 r_1}}^{\hat{H}_1} \overbrace{-\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0 r_2}}^{\hat{H}_2} + \frac{e^2}{4\pi r_{12}}$$

but we are ignoring that term. We shall now show that, if $\psi(r_1)$ is an eigenfunction of $\hat{H}_1$ with energy E_1, and $\psi(r_2)$ is an eigenfunction of $\hat{H}_2$ with energy E_2, then the product $\Psi(r_1,r_2) = \psi(r_1)\psi(r_2)$ is an eigenfunction of the combined hamiltonian $\hat{H}$. To do so we write

$$\begin{aligned}\hat{H}\Psi(r_1,r_2) &= (\hat{H}_1 + \hat{H}_2)\psi(r_1)\psi(r_2) = \hat{H}_1\psi(r_1)\psi(r_2) + \psi(r_1)\hat{H}_2\psi(r_2)\\ &= E_1\psi(r_1)\psi(r_2) + \psi(r_1)E_2\psi(r_2) = (E_1 + E_2)\psi(r_1)\psi(r_2)\\ &= E\Psi(r_1,r_2)\end{aligned}$$

where $E = E_1 + E_2$. This is the result we need to prove. However, if the electrons interact (as they do in fact), then the proof fails.

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Atomic structure

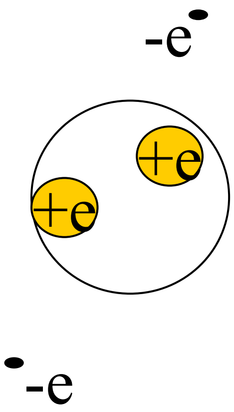
The structures of many-electron atoms

ELIO

(a) The helium atom

The orbital approximation allows us to express the electronic structure of an atom by reporting its **configuration**, a statement of its occupied orbitals (usually, but not necessarily, in its ground state). Thus, as the ground state of a hydrogenic atom consists of the single electron in a 1s orbital, we report its configuration as $1s^1$ (read 'one-ess-one').

A He atom has two electrons. We can imagine forming the atom by adding the electrons in succession to the orbitals of the bare nucleus (of charge $2e$). The first electron occupies a 1s hydrogenic orbital, but because $Z = 2$ that orbital is more compact than in H itself. The second electron joins the first in the 1s orbital, so the electron configuration of the ground state of He is $1s^2$.



Atomic structure

The structures of many-electron atoms

ELIO e LITIO e Principio di PAULI - 1

(b) The Pauli principle

Lithium, with $Z = 3$, has three electrons. The first two occupy a 1s orbital drawn even more closely than in He around the more highly charged nucleus. The third electron, however, does not join the first two in the 1s orbital because that configuration is forbidden by the **Pauli exclusion principle**:

> No more than two electrons may occupy any given orbital, and if two do occupy one orbital, then their spins must be paired.

Pauli exclusion principle

Electrons with paired spins, denoted ↑↓, have zero net spin angular momentum because the spin of one electron is cancelled by the spin of the other. Specifically, one electron has $m_s = +\frac{1}{2}$, the other has $m_s = -\frac{1}{2}$, and they are orientated on their respective cones so that the resultant spin is zero (Fig. 9.18). The exclusion principle is the key to the structure of complex atoms, to chemical periodicity, and to molecular structure. It was proposed by Wolfgang Pauli in 1924 when he was trying to account for the absence of some lines in the spectrum of helium. Later he was able to derive a very general form of the principle from theoretical considerations.

Atomic structure

The structures of many-electron atoms

ELIO e LITIO e Principio di PAULI - 2

The Pauli exclusion principle in fact applies to any pair of identical fermions (particles with half integral spin). Thus it applies to protons, neutrons, and ^{13}C nuclei (all of which have spin $\frac{1}{2}$) and to ^{35}Cl nuclei (which have spin $\frac{3}{2}$). It does not apply to identical bosons (particles with integral spin), which include photons (spin 1), ^{12}C nuclei (spin 0). Any number of identical bosons may occupy the same state (that is, be described by the same wavefunction).

PROTONI , NEUTRONI **Fermioni**
NUCLEI di ^{13}C (spin nucleare I=½)
NUCLEI di ^{35}Cl (spin nucleare I=3/2)
NUCLEI di ^{23}Na (spin nucleare I=3/2)

FOTONI **Bosoni**
NUCLEI di ^{12}C (spin nucleare I=0)
NUCLEI di ^{14}N (spin nucleare I=1)
NUCLEI di ^{2}H (spin nucleare I=1)

Atomic structure

The structures of many-electron atoms

ELIO e LITIO e Principio di PAULI - 2

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The Pauli *exclusion* principle is a special case of a general statement called the **Pauli principle**:

> When the labels of any two identical fermions are exchanged, the total wavefunction changes sign; when the labels of any two identical bosons are exchanged, the sign of the total wavefunction remains the same.

Pauli principle

By 'total wavefunction' is meant the entire wavefunction, including the spin of the particles. To see that the Pauli principle implies the Pauli exclusion principle, we consider the wavefunction for two electrons $\psi(1,2)$. The Pauli principle implies that it is a fact of nature (which has its roots in the theory of relativity) that the wavefunction must change sign if we interchange the labels 1 and 2 wherever they occur in the function:

$$\Psi(2,1) = -\Psi(1,2) \qquad (9.27)$$

Atomic structure

The structures of many-electron atoms

ELIO e LITIO e Principio di PAULI - 3

Suppose the two electrons in an atom occupy an orbital ψ, then in the orbital approximation the overall wavefunction is $\psi(1)\psi(2)$. To apply the Pauli principle, we must deal with the total wavefunction, the wavefunction including spin. There are several

possibilities for two spins: both α, denoted $\alpha(1)\alpha(2)$, both β, denoted $\beta(1)\beta(2)$, and one α the other β, denoted either $\alpha(1)\beta(2)$ or $\alpha(2)\beta(1)$. Because we cannot tell which electron is α and which is β, in the last case it is appropriate to express the spin states as the (normalized) linear combinations

$$\begin{aligned}\sigma_+(1,2) &= (1/2^{1/2})\{\alpha(1)\beta(2)+\beta(1)\alpha(2)\}\\ \sigma_-(1,2) &= (1/2^{1/2})\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\}\end{aligned} \qquad (9.28)$$

These combinations allow one spin to be α and the other β with equal probability. The total wavefunction of the system is therefore the product of the orbital part and one of the four spin states:

$$\begin{aligned}&\psi(1)\psi(2)\alpha(1)\alpha(2) \qquad &&\psi(1)\psi(2)\beta(1)\beta(2)\\ &\psi(1)\psi(2)\sigma_+(1,2) \qquad &&\psi(1)\psi(2)\sigma_-(1,2)\end{aligned} \qquad (9.29)$$

Atomic structure

The structures of many-electron atoms

ELIO e LITIO e Principio di PAULI - 3

The Pauli principle says that, for a wavefunction to be acceptable (for electrons), it must change sign when the electrons are exchanged. In each case, exchanging the labels 1 and 2 converts the factor $\psi(1)\psi(2)$ into $\psi(2)\psi(1)$, which is the same, because the order of multiplying the functions does not change the value of the product. The same is true of $\alpha(1)\alpha(2)$ and $\beta(1)\beta(2)$. Therefore, the first two overall products are not allowed, because they do not change sign. The combination $\sigma_+(1,2)$ changes to

$$\sigma_+(2,1) = (1/2^{1/2})\{\alpha(2)\beta(1) + \beta(2)\alpha(1)\} = \sigma_+(1,2)$$

because it is simply the original function written in a different order. The third overall product is therefore also disallowed. Finally, consider $\sigma_-(1,2)$:

$$\begin{aligned}\sigma_-(2,1) &= (1/2^{1/2})\{\alpha(2)\beta(1) - \beta(2)\alpha(1)\}\\ &= -(1/2^{1/2})\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} = -\sigma_-(1,2)\end{aligned}$$

This combination does change sign (it is 'antisymmetric'). The product $\psi(1)\psi(2)\sigma_-(1,2)$ also changes sign under particle exchange, and therefore it is acceptable.

Now we see that only one of the four possible states is allowed by the Pauli principle, and the one that survives has paired α and β spins. This is the content of the Pauli exclusion principle. The exclusion principle is irrelevant when the orbitals occupied by the electrons are different, and both electrons may then have (but need not have) the same spin state. Nevertheless, even then the overall wavefunction must still be antisymmetric overall, and must still satisfy the Pauli principle itself.

Struttura Atomica

Atomi a 2 o più elettroni

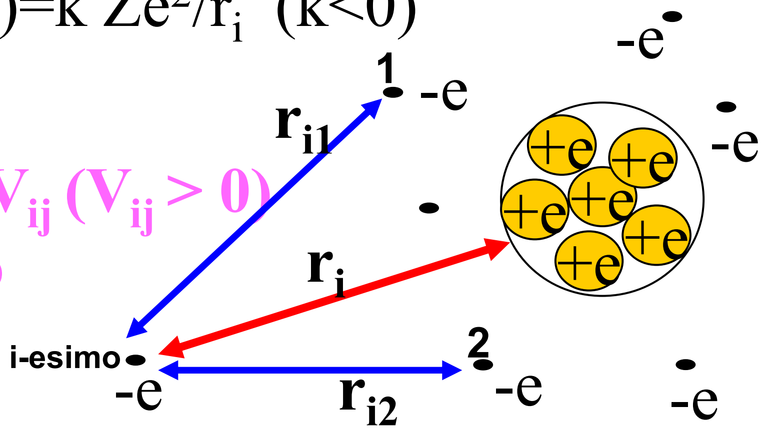
$$\hat{H}\Psi = E\Psi$$

equazione di Schrödinger

Ogni elettrone i-esimo di massa m :

- è soggetto all'energia potenziale $V_i(r_i)=k\ Ze^2/r_i$ $(k<0)$ di attrazione da parte del nucleo.

- **è soggetto all'energia potenziale $\Sigma_j V_{ij}$ $(V_{ij} > 0)$ di repulsione da parte di ogni altro elettrone j-esimo ($i \neq j$).**



- inoltre possiede energia cinetica

L'operatore Ĥ e l'eq. di Schrödinger contengono i termini corrispondenti di energia potenziale e cinetica

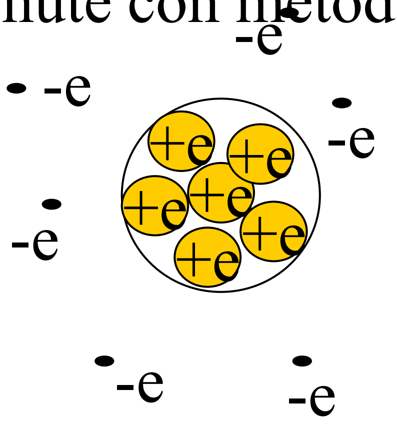
$$-\frac{\hbar^2}{2m}\nabla^2\Psi + V(r)\Psi = E\Psi$$

L'equazione di Schrödinger non si può risolvere in modo esatto.

Atomi a 2 o più elettroni

$$\boxed{\hat{H}\Psi = E\Psi}$$ equazione di Schrödinger

Non è possibile trovare delle soluzioni analitiche dell’eq.di Schrödinger.
Si usano delle soluzioni approssimate (ad esempio ottenute con metodi numerici) e che vengono chiamate ancora



ORBITALI ATOMICI

- caratterizzati ancora dai tre numeri quantici n, ℓ, m_ℓ
- ognuno degli elettroni ha ancora $s = ½$ ed $m_s = -½$, ½

L’espressione per l’energia

$$\xcancel{E_n = -\frac{Z^2 \mu e^4}{32\pi^2 \varepsilon_0^2 \hbar^2} \frac{1}{n^2}}$$

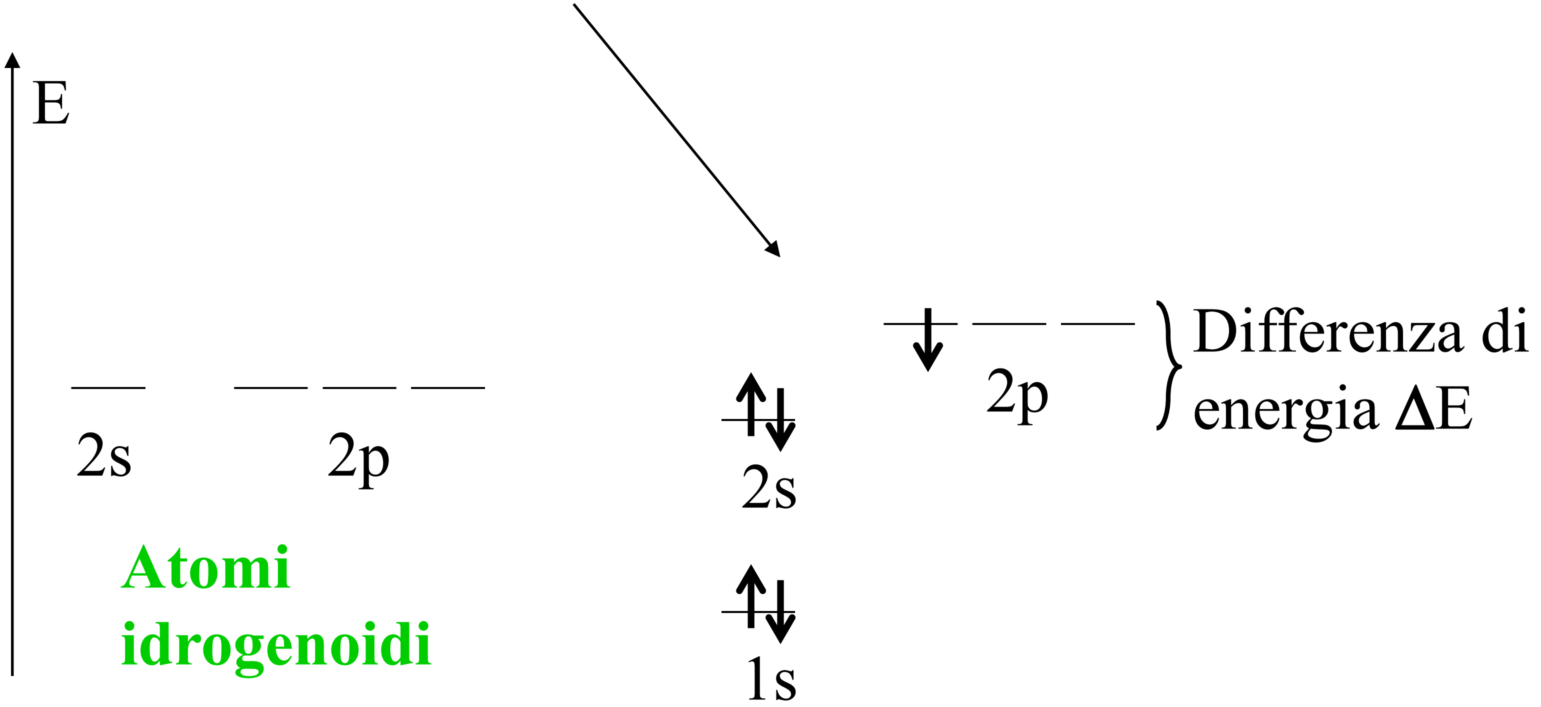
non è più valida

Atomi a 2 o più elettroni

$$\boxed{\hat{H}\Psi = E\Psi}$$ equazione di Schrödinger

Effetto della repulsione elettrostatica sull'elettrone i-esimo da parte di ogni altro elettrone j-esimo

Esempio: l'atomo di Boro (Z=5) ; config. elettronica $1s^2\ 2s^2\ 2p^1$



Differenza di energia ΔE

Atomi idrogenoidi

Atomo a 2 o più elettroni

Struttura Atomica

$$\hat{H}\Psi = E\Psi$$

Atomi a 2 o più elettroni

equazione di Schrödinger

Effetto della repulsione elettrostatica sull'elettrone i-esimo da parte di ogni altro elettrone j-esimo

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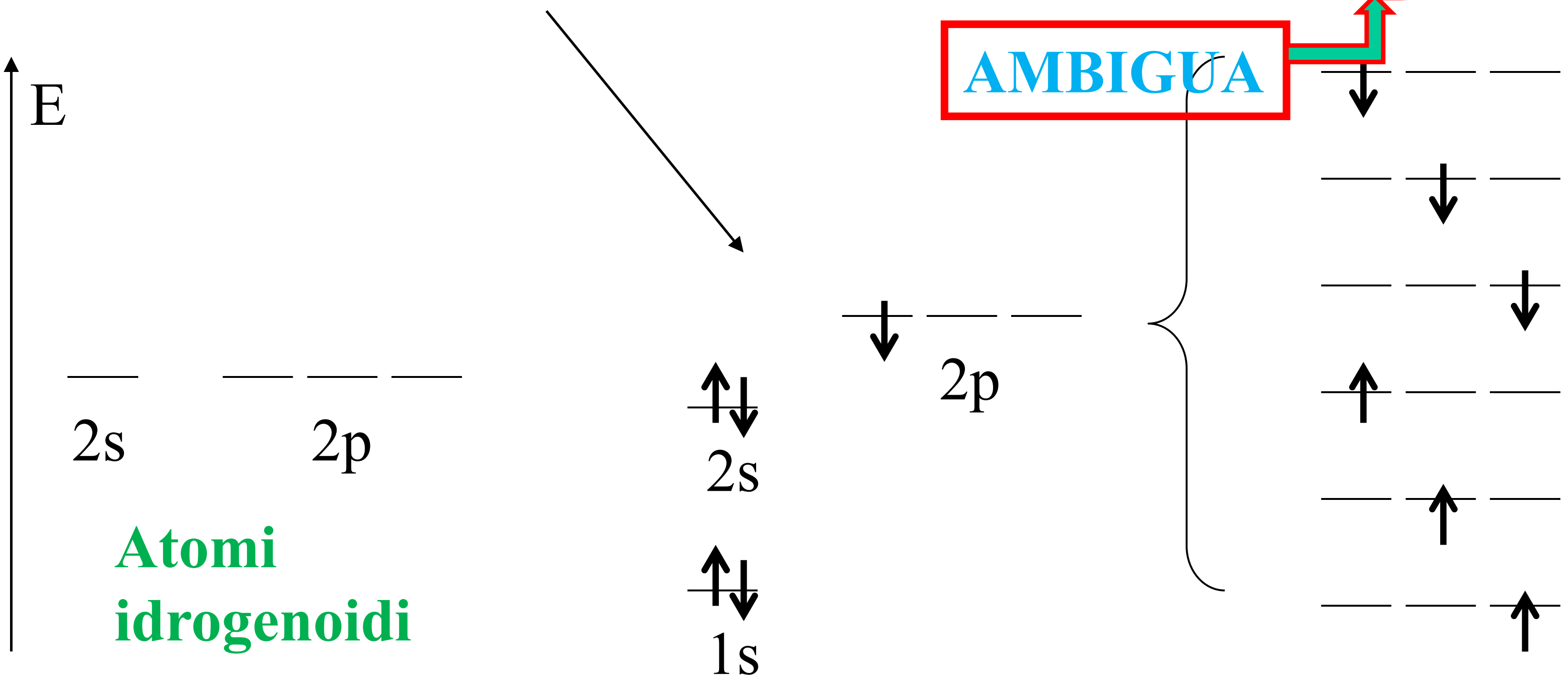
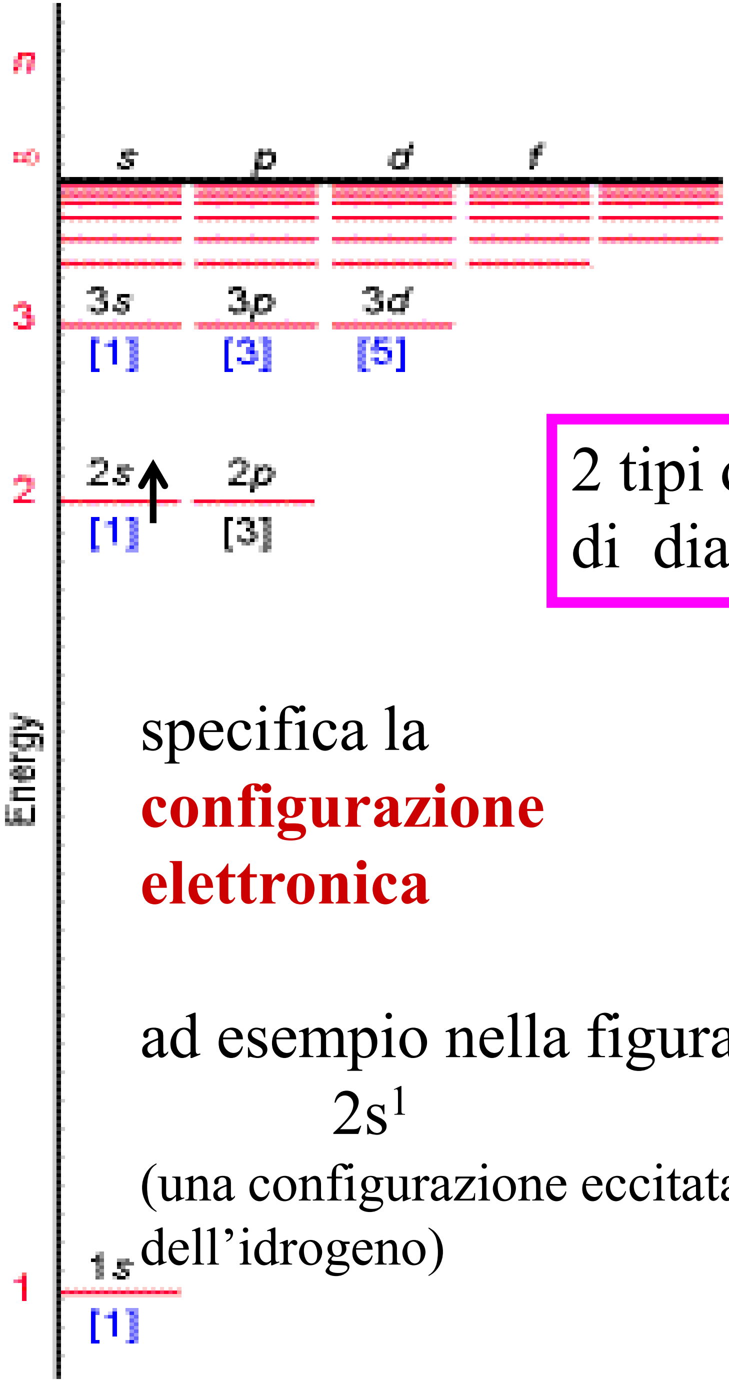


Atomi idrogenoidi

Atomo a 2 o più elettroni

6 stati elettronici differenti

Diagramma di Grotrian per l'atomo di sodio



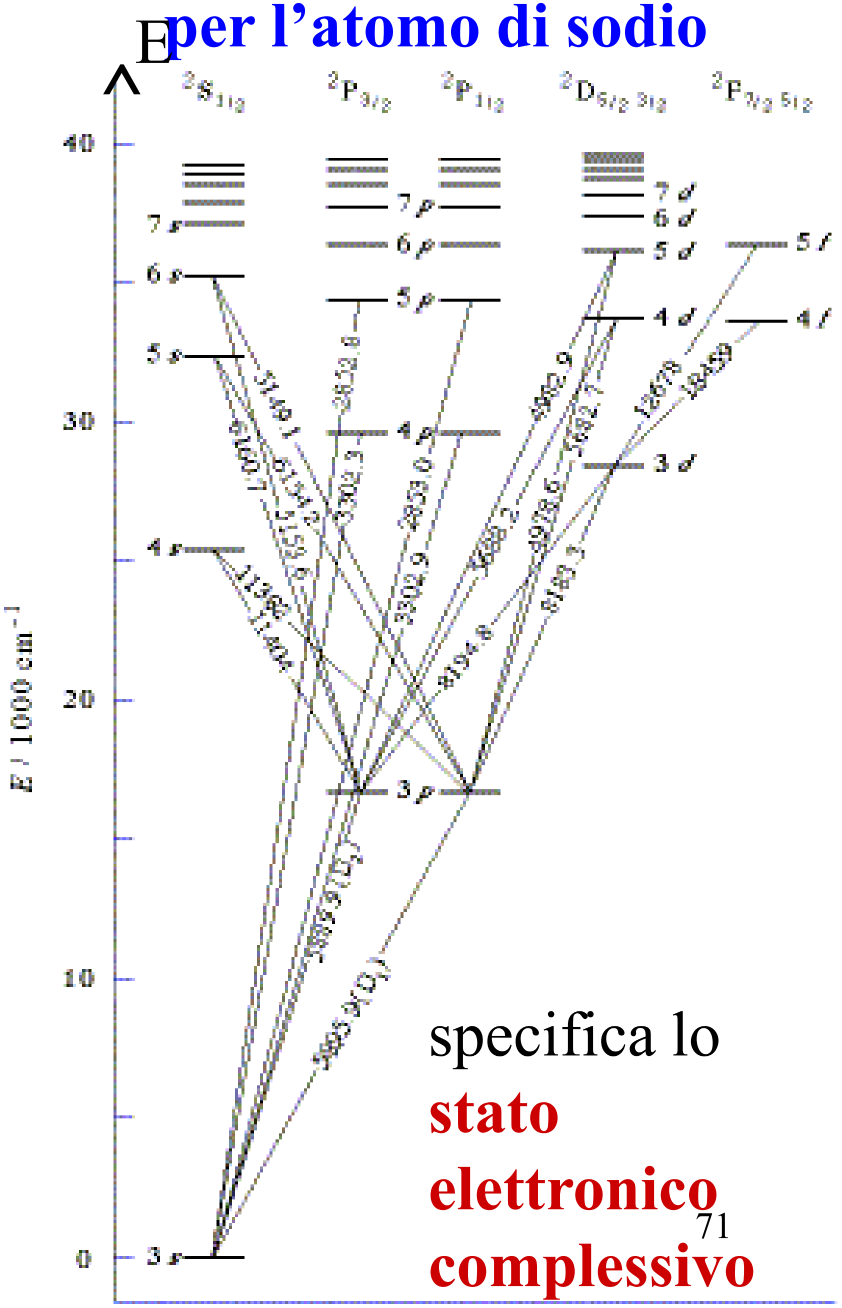
2 tipi diversi
di diagrammi

specifica la **configurazione elettronica**

ad esempio nella figura:

$2s^1$

(una configurazione eccitata dell'idrogeno)



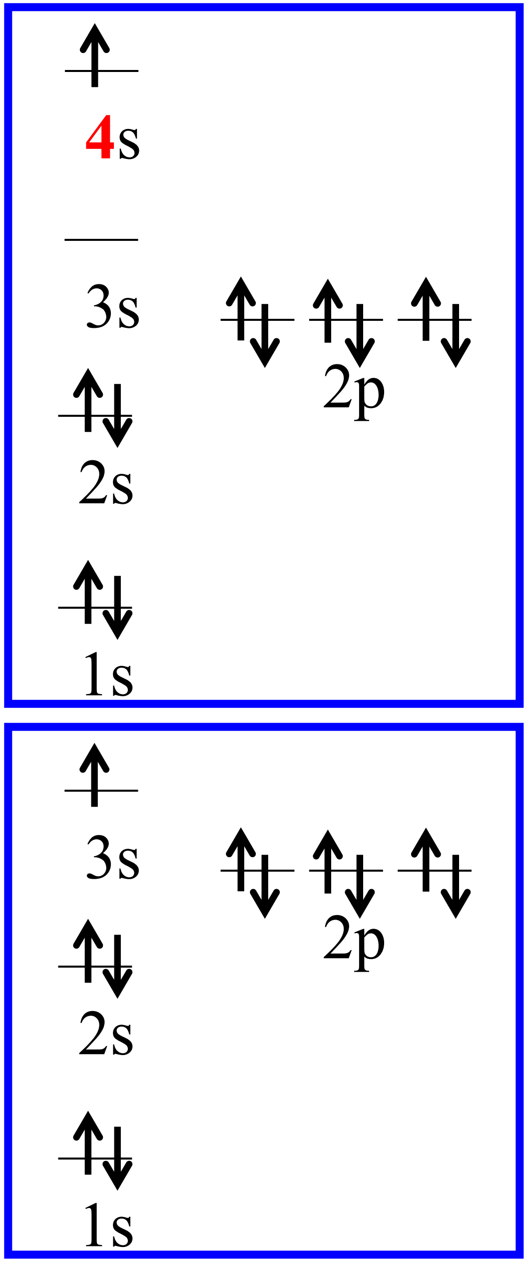
specifica lo **stato elettronico complessivo**

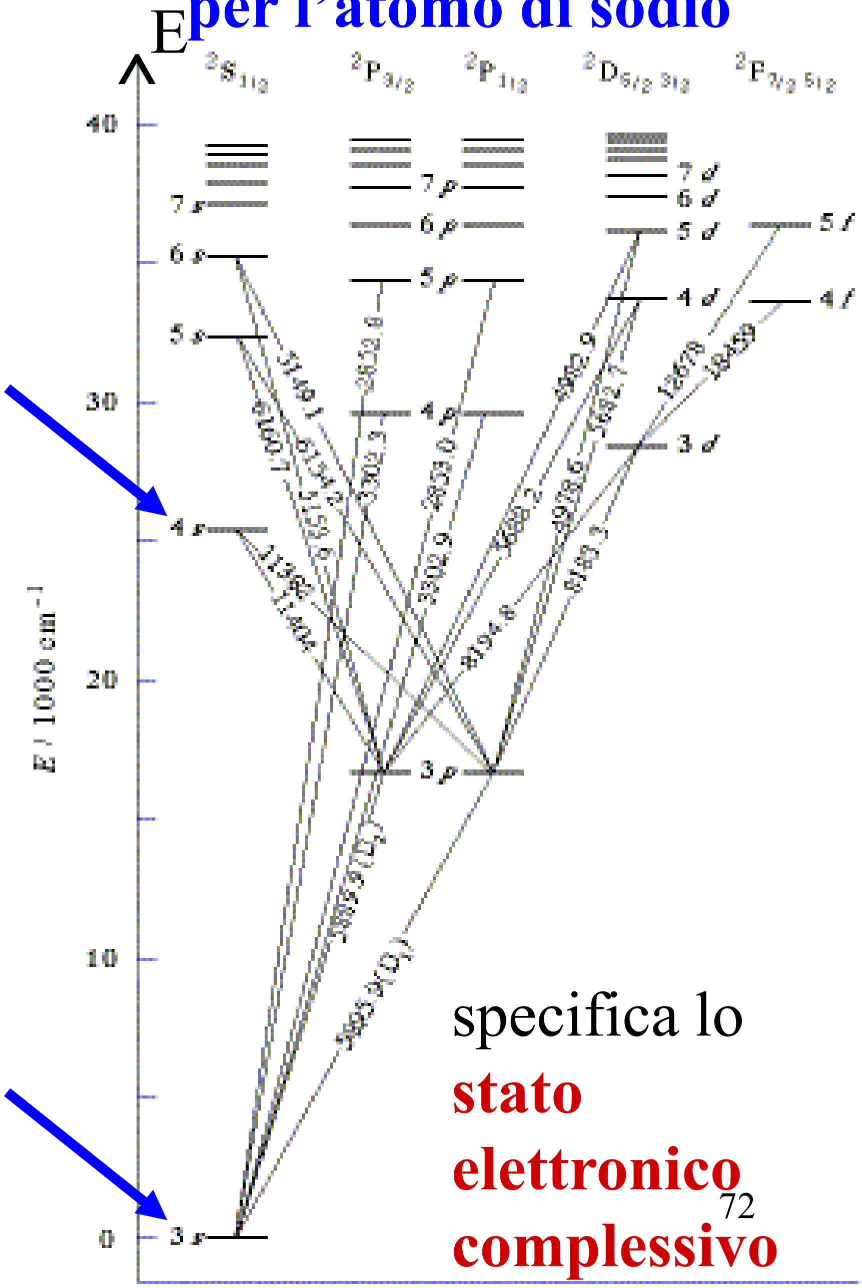
Esempio: l'atomo di Sodio – Na (Z=11)

Diagramma di Grotrian per l'atomo di sodio

Una config. elettronica eccitata: 1s^2 2s^2 2p^6 **4**s^1

configuraz. elettronica fondamentale: 1s^2 2s^2 2p^6 3s^1





specifica lo **stato elettronico complessivo**

ATOMI A MOLTI ELETTRONI

Determinanti di SLATER
Penetrazione fino al nucleo degli orbitali
Schermaggio della carica nucleare
AufbauPrinzip - Regola di Hund

Chimica Fisica 2

Laurea Tri. Chim. In. 2022-23

Lun 8-5-2023

Prof. Antonio Toffoletti

Atomic structure

The structures of many-electron atoms

ELIO e LITIO e Principio di PAULI - 3

The Pauli principle says that, for a wavefunction to be acceptable (for electrons), it must change sign when the electrons are exchanged. In each case, exchanging the labels 1 and 2 converts the factor $\psi(1)\psi(2)$ into $\psi(2)\psi(1)$, which is the same, because the order of multiplying the functions does not change the value of the product. The same is true of $\alpha(1)\alpha(2)$ and $\beta(1)\beta(2)$. Therefore, the first two overall products are not allowed, because they do not change sign. The combination $\sigma_+(1,2)$ changes to

$$\sigma_+(2,1) = (1/2^{1/2})\{\alpha(2)\beta(1) + \beta(2)\alpha(1)\} = \sigma_+(1,2)$$

because it is simply the original function written in a different order. The third overall product is therefore also disallowed. Finally, consider $\sigma_-(1,2)$:

$$\begin{aligned}\sigma_-(2,1) &= (1/2^{1/2})\{\alpha(2)\beta(1) - \beta(2)\alpha(1)\}\\ &= -(1/2^{1/2})\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} = -\sigma_-(1,2)\end{aligned}$$

This combination does change sign (it is 'antisymmetric'). The product $\psi(1)\psi(2)\sigma_-(1,2)$ also changes sign under particle exchange, and therefore it is acceptable.

Now we see that only one of the four possible states is allowed by the Pauli principle, and the one that survives has paired α and β spins. This is the content of the Pauli exclusion principle. The exclusion principle is irrelevant when the orbitals occupied by the electrons are different, and both electrons may then have (but need not have) the same spin state. Nevertheless, even then the overall wavefunction must still be antisymmetric overall, and must still satisfy the Pauli principle itself.

Atomic structure

The structures of many-electron atoms

ELIO e LITIO e Principio di PAULI - 3

A final point in this connection is that the acceptable product wavefunction $\psi(1)\psi(2)\sigma\_(1,2)$ can be expressed as a determinant:

$$\frac{1}{2^{1/2}}\begin{vmatrix} \psi(1)\alpha(1) & \psi(2)\alpha(2) \\ \psi(1)\beta(1) & \psi(2)\beta(2) \end{vmatrix} = \frac{1}{2^{1/2}}\{\psi(1)\alpha(1)\psi(2)\beta(2) - \psi(2)\alpha(2)\psi(1)\beta(1)\}$$

$$= \psi(1)\psi(2)\sigma\_(1,2)$$

Any acceptable wavefunction for a closed-shell species can be expressed as a **Slater determinant**, as such determinants are known. In general, for N electrons in orbitals $\psi_a, \psi_b, \ldots$

$$\Psi(1,2,\ldots,N) = \frac{1}{(N!)^{1/2}}\begin{vmatrix} \psi_a(1)\alpha(1) & \psi_a(2)\alpha(2) & \psi_a(3)\alpha(3) & \ldots & \psi_a(N)\alpha(N) \\ \psi_a(1)\beta(1) & \psi_a(2)\beta(2) & \psi_a(3)\beta(3) & \ldots & \psi_a(N)\beta(N) \\ \psi_b(1)\alpha(1) & \psi_a(2)\alpha(2) & \psi_b(3)\alpha(3) & \ldots & \psi_b(N)\alpha(N) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \psi_z(1)\beta(1) & \psi_z(2)\beta(2) & \psi_z(3)\beta(3) & \ldots & \psi_z(N)\beta(N) \end{vmatrix} \tag{9.30a}$$

DETERMINANTE DI SLATER

Atomic structure

The structures of many-electron atoms

ELIO e LITIO e Principio di PAULI - 3

Ogni riga contiene la stessa funzione

Ogni colonna contiene lo stesso elettrone

$$\Psi(1,2,\ldots,N)=\frac{1}{(N!)^{1/2}}\begin{vmatrix} \psi_a(1)\alpha(1) & \psi_a(2)\alpha(2) & \psi_a(3)\alpha(3) & \ldots & \psi_a(N)\alpha(N) \\ \psi_a(1)\beta(1) & \psi_a(2)\beta(2) & \psi_a(3)\beta(3) & \ldots & \psi_a(N)\beta(N) \\ \psi_b(1)\alpha(1) & \psi_a(2)\alpha(2) & \psi_b(3)\alpha(3) & \ldots & \psi_b(N)\alpha(N) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \psi_z(1)\beta(1) & \psi_z(2)\beta(2) & \psi_z(3)\beta(3) & \ldots & \psi_z(N)\beta(N) \end{vmatrix} \quad [9.30a]$$

DETERMINANTE DI SLATER

Atomic structure

The structures of many-electron atoms

ELIO e LITIO e Principio di PAULI - 3

Writing a many-electron wavefunction in this way ensures that it is antisymmetric under the interchange of any pair of electrons, as is explored in Problem 9.25.Because a Slater determinant takes up a lot of space, it is normally reported by writing only its diagonal elements, as in

$$\Psi(1,2,\ldots,N) = \left(\frac{1}{N!}\right)^{1/2} \det|\psi_a^\alpha(1)\psi_a^\beta(2)\psi_b^\alpha(3)\cdots\psi_z^\beta(N)| \qquad [9.30b]$$

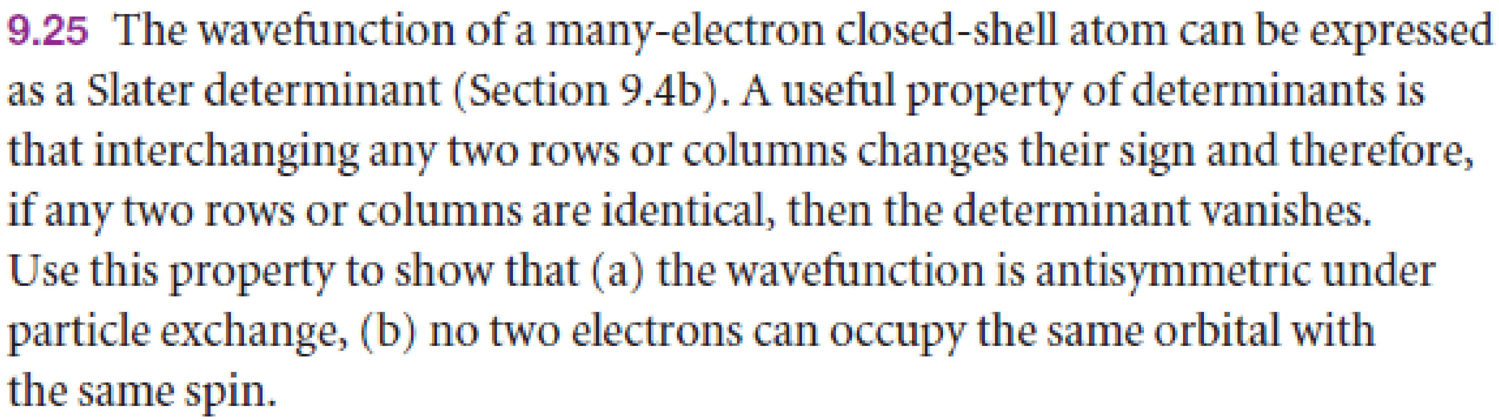
Notation for a Slater determinant

Now we can return to lithium. In Li ($Z = 3$), the third electron cannot enter the 1s orbital because that orbital is already full: we say the K shell is *complete* and that the two electrons form a **closed shell**. Because a similar closed shell is characteristic of the He atom, we denote it [He]. The third electron is excluded from the K shell and must occupy the next available orbital, which is one with $n = 2$ and hence belonging to the L shell. However, we now have to decide whether the next available orbital is the 2s orbital or a 2p orbital, and therefore whether the lowest energy configuration of the atom is [He]$2s^1$ or [He]$2p^1$.

Atomic structure

The structures of many-electron atoms

ELIO e LITIO e Principio di PAULI - 3



9.25 The wavefunction of a many-electron closed-shell atom can be expressed as a Slater determinant (Section 9.4b). A useful property of determinants is that interchanging any two rows or columns changes their sign and therefore, if any two rows or columns are identical, then the determinant vanishes. Use this property to show that (a) the wavefunction is antisymmetric under particle exchange, (b) no two electrons can occupy the same orbital with the same spin.

Atomic structure

The structures of many-electron atoms

ELIO e LITIO e Principio di PAULI - 3

ESERCIZIO 9.25

9.25 The wavefunction of a many-electron closed-shell atom can be expressed as a Slater determinant (Section 9.4b). A useful property of determinants is that interchanging any two rows or columns changes their sign and therefore, if any two rows or columns are identical, then the determinant vanishes. Use this property to show that (a) the wavefunction is antisymmetric under particle exchange, (b) no two electrons can occupy the same orbital with the same spin.

$$\begin{matrix} 1 & 0 & 5 \\ 2/3 & 2 & 1 \\ 1 & 3 & 3 \end{matrix} = 1 \times [(2 \times 3)-(3 \times 1)] + (-0) \times [(2/3 \times 3)-(1 \times 1)] + 5 \times [(2/3 \times 3)-(1 \times 2)]$$

$$= 1 \times 3 + 0 + 0 = 3$$

$$\begin{matrix} 5 & 0 & 1 \\ 1 & 2 & 2/3 \\ 3 & 3 & 1 \end{matrix} = 5 \times [(2 \times 1)-(3 \times 2/3)] + (-0) \times [(1 \times 1)-(3 \times 2/3)] + 1 \times [(1 \times 3)-(3 \times 2)]$$

$$= 5 \times (0) + 0 + 1 \times (-3) = -3$$

Atomic structure

Penetration and shielding

ATOMI A MOLTI ELETTRONI

Unlike in hydrogenic atoms, the 2s and 2p orbitals (and, in general, all subshells of a given shell) are not degenerate in many-electron atoms. An electron in a many-electron atom experiences a Coulombic repulsion from all the other electrons present. If it is at a distance *r* from the nucleus, it experiences an average repulsion that can be represented by a point negative charge located at the nucleus and equal in magnitude to the total charge of the electrons within a sphere of radius *r* (Fig. 9.19). The effect of this point negative charge, when averaged over all the locations of the electron, is to reduce the full charge of the nucleus from Ze to $Z_{\text{eff}}e$, the **effective nuclear charge**. In everyday parlance, Z_{eff} itself is commonly referred to as the 'effective nuclear charge'. We say that the electron experiences a **shielded** nuclear charge, and the difference between Z and Z_{eff} is called the **shielding constant**, σ:

$$Z_{\text{eff}} = Z - \sigma \qquad [9.31]$$

Effective nuclear charge

The electrons do not actually 'block' the full Coulombic attraction of the nucleus: the shielding constant is simply a way of expressing the net outcome of the nuclear attraction and the electronic repulsions in terms of a single equivalent charge at the centre of the atom.

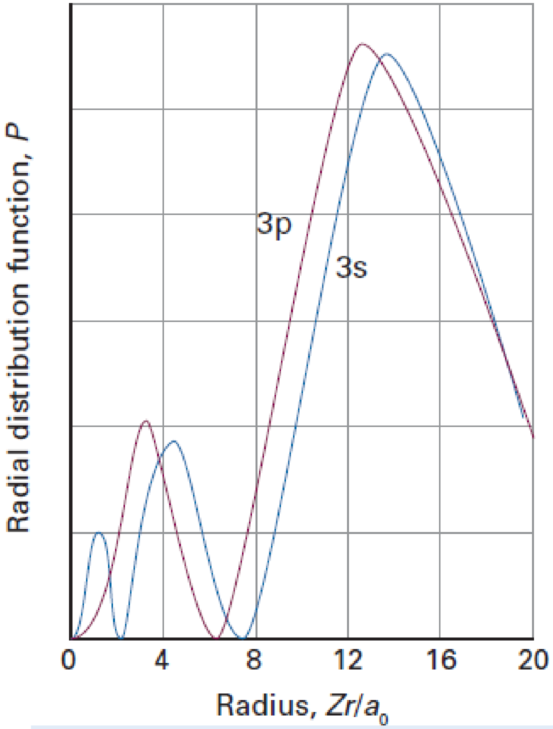
Atomic structure

Penetration and shielding

ATOMI A MOLTI ELETTRONI

The shielding constant is different for s and p electrons because they have different radial distributions (see the Figure). An s electron has a greater **penetration** through inner shells than a p electron, in the sense that it is more likely to be found close to the nucleus than a p electron of the same shell (the wave-function of a p orbital, remember, is zero at the nucleus). Because only electrons inside the sphere defined by the location of the electron contribute to shielding, an s electron experiences less shielding than a p electron. Consequently, by the combined effects of penetration and shielding, an s electron is more tightly bound than a p electron of the same shell. Similarly, a d electron penetrates less than a p electron of the same shell (recall that the wavefunction of a d orbital varies as r^2 close to the nucleus, whereas a p orbital varies as r), and therefore experiences more shielding.

Shielding constants for different types of electrons in atoms have been calculated from their wavefunctions obtained by numerical solution of the Schrödinger equation for the atom (see the Table). We see that, in general, valence-shell s electrons do experience higher effective nuclear charges than p electrons, although there are some discrepancies.



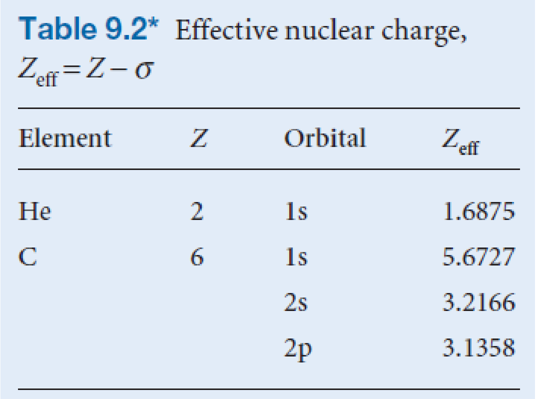


Table 9.2* Effective nuclear charge, $Z_{\mathrm{eff}} = Z - \sigma$

Element	Z	Orbital	Z_{eff}
He	2	1s	1.6875
C	6	1s	5.6727
		2s	3.2166
		2p	3.1358

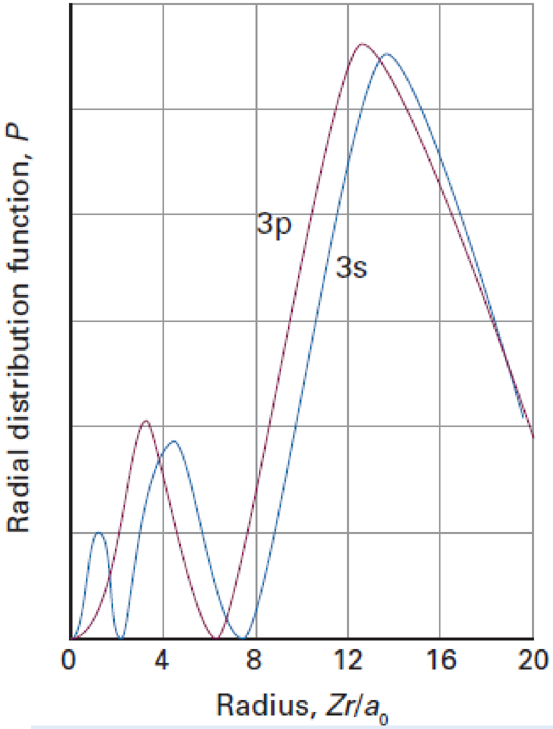
Atomic structure

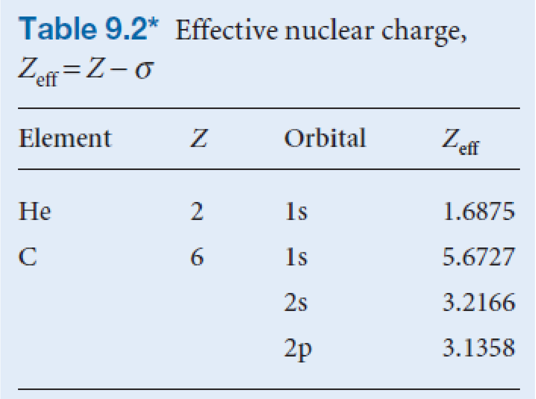
Penetration and shielding

ATOMI A MOLTI ELETTRONI

The consequence of penetration and shielding is that the energies of subshells of a shell in a many-electron atom (those with the same values of *n* but different values of *l*) in general lie in the order s < p < d < f. The individual orbitals of a given subshell (those with the same value of *l* but different values of *ml*) remain degenerate because they all have the same radial characteristics and so experience the same effective nuclear charge.

We can now complete the Li story. Because the shell with $n =$ 2 consists of two nondegenerate subshells, with the 2s orbital lower in energy than the three 2p orbitals, the third electron occupies the 2s orbital. This occupation results in the ground-state configuration $1s^2 2s^1$, with the central nucleus surrounded by a complete helium-like shell of two 1s electrons, and around that a more diffuse 2s electron. The electrons in the outermost shell of an atom in its ground state are called the **valence electrons** because they are largely responsible for the chemical bonds that the atom forms. Thus, the valence electron in Li is a 2s electron and its other two electrons belong to its core.





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Atomic structure

The building-up principle

ATOMI A MOLTI ELETTRONI

The extension of this argument is called the **building-up principle**, or the *Aufbau principle*, from the German word for building up, which will be familiar from introductory courses. In brief, we imagine the bare nucleus of atomic number *Z*, and then feed into the orbitals *Z* electrons in succession. The order of occupation is

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s

and each orbital may accommodate up to two electrons. As an example, consider the carbon atom, for which $Z = 6$ and there are six electrons to accommodate. Two electrons enter and fill the 1s orbital, two enter and fill the 2s orbital, leaving two electrons to occupy the orbitals of the 2p subshell. Hence the ground-state configuration of C is $1s^2 2s^2 2p^2$, or more succinctly $[He]2s^2 2p^2$, with [He] the helium-like $1s^2$ core.

However, we can be more precise: we can expect the last two electrons to occupy different 2p orbitals because they will then be further apart on average and repel each other less than if they were in the same orbital. Thus, one electron can be thought of as occupying the $2p_x$ orbital and the other the $2p_y$ orbital (the *x*, *y*, *z* designation is arbitrary, and it would be equally valid to use the complex forms of these orbitals), and the lowest energy configuration of the atom is $[He]2s^2 2p^1_x 2p^1_y$.

Atomic structure

The building-up principle

The same rule applies whenever degenerate orbitals of a subshell are av-ailable for occupation. Thus, another rule of the building-up principle is:

Electrons occupy different orbitals of a given subshell before doubly occupying any one of them.

For instance, nitrogen ($Z = 7$) has the configuration $[\mathrm{He}]2s^22p^1_x\ 2p^1_y\ 2p^1_z$, and only when we get to oxygen ($Z = 8$) is a 2p orbital doubly occupied, giving $[\mathrm{He}]2s^22p^2_x2p^1_y\ 2p^1_z$.
When electrons occupy orbitals singly, we invoke **Hund's maximum multiplicity rule**:

An atom in its ground state adopts a configuration with the greatest number of unpaired electrons.

The explanation of Hund's rule is subtle, but it reflects the quantum mechanical property of **spin correlation**, that, as we demonstrate in the following *Justification*, electrons with parallel spins behave as if they have a tendency to stay well apart, and hence repel each other less. In essence, the effect of spin correlation is to allow the atom to shrink slightly, so the electron–nucleus interaction is improved when the spins are parallel. We can now conclude that, in the ground state of the carbon atom, the two 2p electrons have the same spin, that all three 2p electrons in the N atoms have the same spin (that is, they are parallel), and that the two 2p electrons in different orbitals in the O atom have the same spin (the two in the $2p_x$ orbital are necessarily paired).

Atomic structure

The building-up principle

ATOMI A MOLTI ELETTRONI

Justification 9.6 *Spin correlation*

Suppose electron 1 is described by a wavefunction $\psi_a(r_1)$ and electron 2 is described by a wavefunction $\psi_b(r_2)$; then, in the orbital approximation, the joint wavefunction of the electrons is the product $\Psi = \psi_a(r_1)\psi_b(r_2)$. However, this wavefunction is not acceptable, because it suggests that we know which electron is in which orbital, whereas we cannot keep track of electrons. According to quantum mechanics, the correct description is either of the two following wavefunctions:

$$\Psi_\pm = (1/2^{1/2})\{\psi_a(r_1)\psi_b(r_2) \pm \psi_b(r_1)\psi_a(r_2)\}$$

According to the Pauli principle, because Ψ_+ is symmetrical under particle interchange, it must be multiplied by an antisymmetric spin function (the one denoted σ_-). That combination corresponds to a spin-paired state. Conversely, Ψ_- is antisymmetric, so it must be multiplied by one of the three symmetric spin states. These three symmetric states correspond to electrons with parallel spins (see Section 9.8 for an explanation).

Now consider the values of the two combinations when one electron approaches another, and $r_1 = r_2$. We see that Ψ_- vanishes, which means that there is zero probability of finding the two electrons at the same point in space when they have parallel spins. The other combination does not vanish when the two electrons are at the same point in space. Because the two electrons have different relative spatial distributions depending on whether their spins are parallel or not, it follows that their Coulombic interaction is different, and hence that the two states have different energies.

ATOMI A MOLTI ELETTRONI

AufbauPrinzip - Regola di Hund

Energie di Ionizzazione e Affinità elettroniche

Metodo SCF

Momenti angolari di più elettroni

Termini spettroscopici

Chimica Fisica 2

Laurea Tri. Chim. In. 2020-21

Mar 13-4-2021

Prof. Antonio Toffoletti

Atomic structure

The building-up principle

ATOMI A MOLTI ELETTRONI

Esame relativamente dettagliato della configurazione elettronica degli elementi fino a Kr e di alcuni ioni di metalli del blocco d.

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Atomic structure

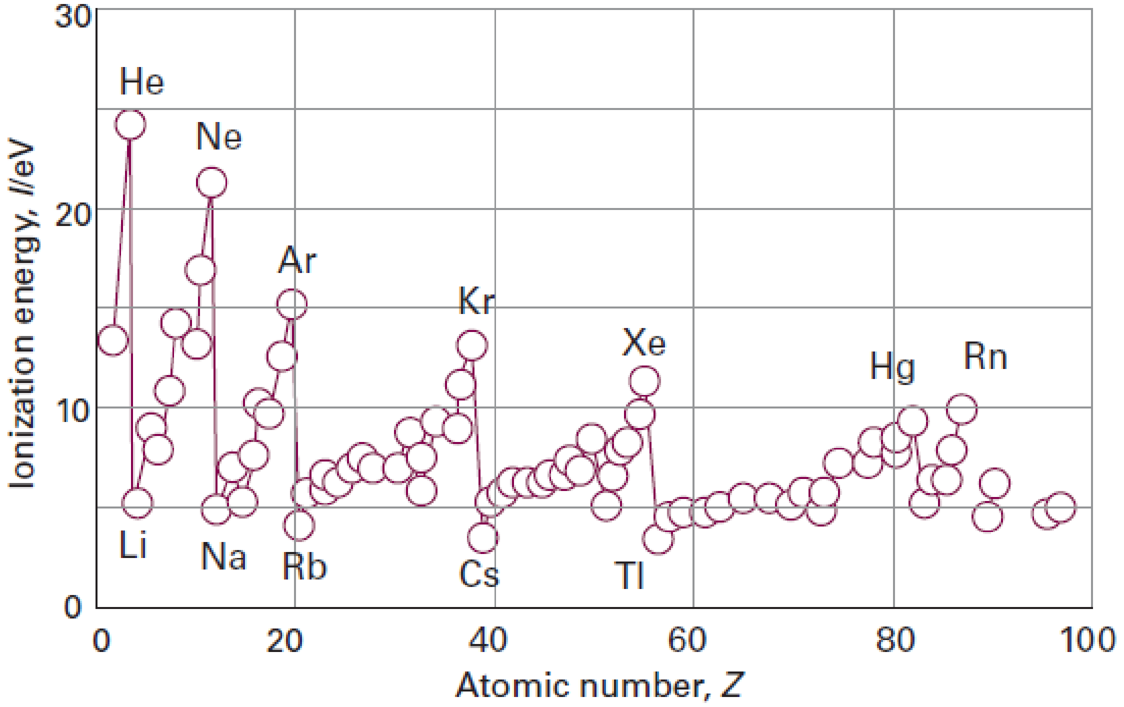
Ionization energies and electron affinities

ATOMI A MOLTI ELETTRONI

The minimum energy necessary to remove an electron from a many-electron atom in the gas phase is the **first ionization energy**, I_1, of the element. The **second ionization energy**, I_2, is the minimum energy needed to remove a second electron (from the singly charged cation). The variation of the first ionization energy through the periodic table is shown in Fig. 9.22 and some numerical values are given in Table 9.3. In thermodynamic calculations we often need the **standard enthalpy of ionization**, $\Delta_{\text{ion}}H^{\ominus}$. As shown in the following *Justification*, the two are related by

$$\Delta_{\text{ion}}H^{\ominus}(T) = I_1 + \tfrac{5}{2}RT \qquad (9.32)$$

Element	$I_1/(\text{kJ mol}^{-1})$	$I_2/(\text{kJ mol}^{-1})$
H	1312	
He	2372	5251
Mg	738	1451
Na	496	4562



Atomic structure

Ionization energies and electron affinities

ATOMI A MOLTI ELETTRONI

At 298 K, the difference between the ionization enthalpy and the corresponding ionization energy is 6.20 kJ mol^{-1}.

Justification 9.7 *The ionization enthalpy and the ionization energy*

It follows from Kirchhoff's law (Section 2.9 and eqn 2.36) that the reaction enthalpy for

$$\mathrm{M(g)} \rightarrow \mathrm{M^{+}(g)} + \mathrm{e^{-}(g)}$$

at a temperature T is related to the value at $T = 0$ by

$$\Delta_r H^{\ominus}(T) = \Delta_r H^{\ominus}(0) + \int_0^T \Delta_r C_p^{\ominus} \mathrm{d}T$$

The molar constant-pressure heat capacity of each species in the reaction is $\frac{5}{2}R$, so $\Delta_r C_p^{\ominus} = +\frac{5}{2}R$. The integral in this expression therefore evaluates to $+\frac{5}{2}RT$. The reaction enthalpy at $T = 0$ is the same as the (molar) ionization energy, I_1. Equation 9.32 then follows. The same expression applies to each successive ionization step, so the overall ionization enthalpy for the formation of $\mathrm{M^{2+}}$ is

$$\Delta_r H^{\ominus}(T) = I_1 + I_2 + 5RT$$

Atomic structure

Ionization energies and electron affinities

ATOMI A MOLTI ELETTRONI

The **electron affinity**, E_{ea}, is the energy released when an electron attaches to a gas-phase atom (Table 9.4). In a common, logical (given its name), but not universal convention (which we adopt), the electron affinity is positive if energy is released when the electron attaches to the atom (that is, $E_{ea} > 0$ implies that electron attachment is exothermic). It follows from a similar argument to that given in the *Justification* above that the **standard enthalpy of electron gain**, $\Delta_{eg}H^{\ominus}$, at a temperature T is related to the electron affinity by

$$\Delta_{eg}H^{\ominus}(T) = -E_{ea} - \tfrac{5}{2}RT \qquad (9.33)$$

Note the change of sign. In typical thermodynamic cycles the $\tfrac{5}{2}RT$ that appears in eqn 9.32 cancels that in eqn 9.33, so ionization energies and electron affinities can be used directly. A final preliminary point is that the electron-gain enthalpy of a species X is the negative of the ionization enthalpy of its negative ion:

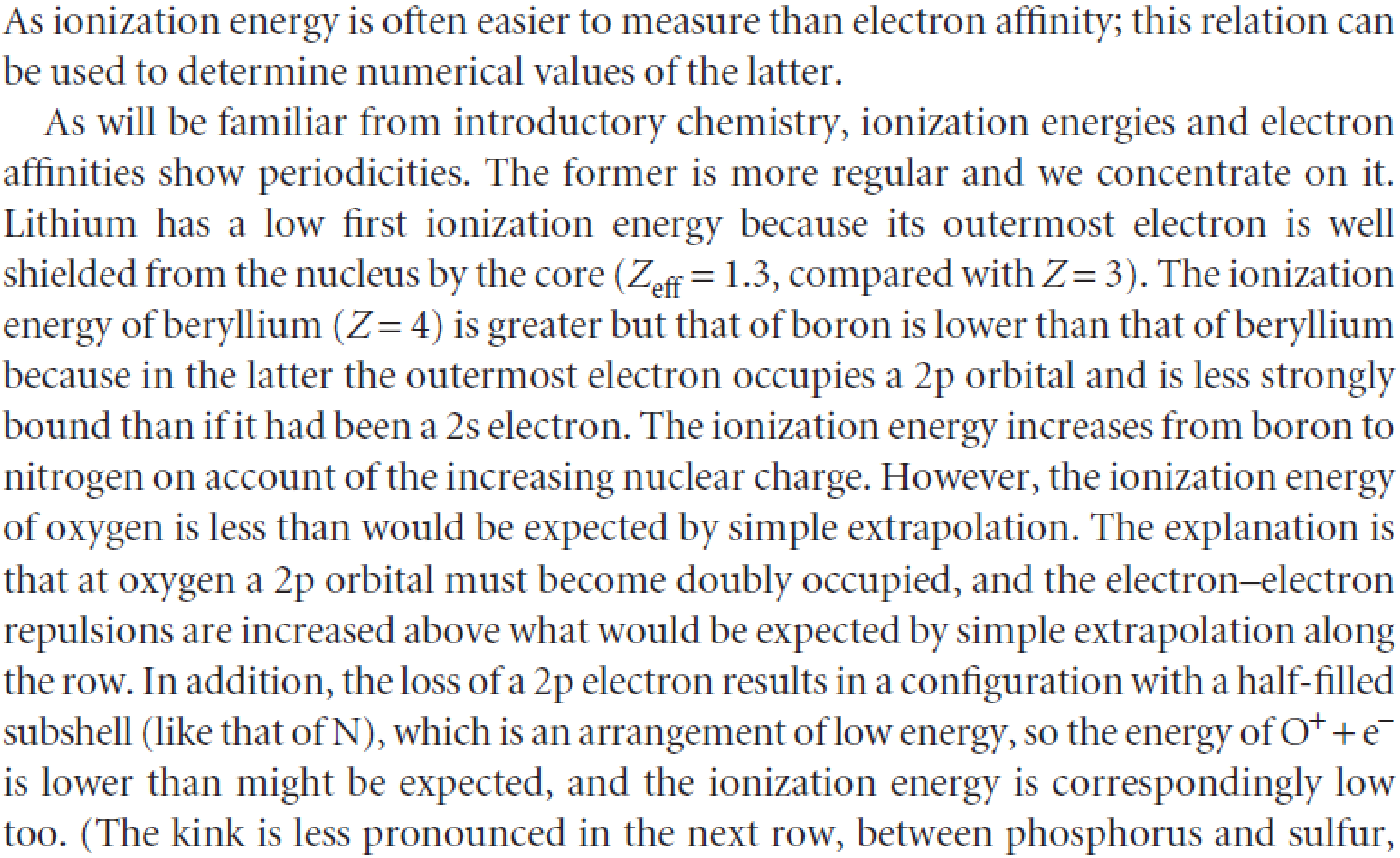
$$\Delta_{eg}H^{\ominus}(\mathrm{X}) = -\Delta_{ion}H^{\ominus}(\mathrm{X}^-) \qquad (9.34)$$

Table 9.4* Electron affinities, $E_a/(\mathrm{kJ\ mol^{-1}})$

Cl	349		
F	322		
H	73		
O	141	O^-	–844

Atomic structure

Ionization energies and electron affinities



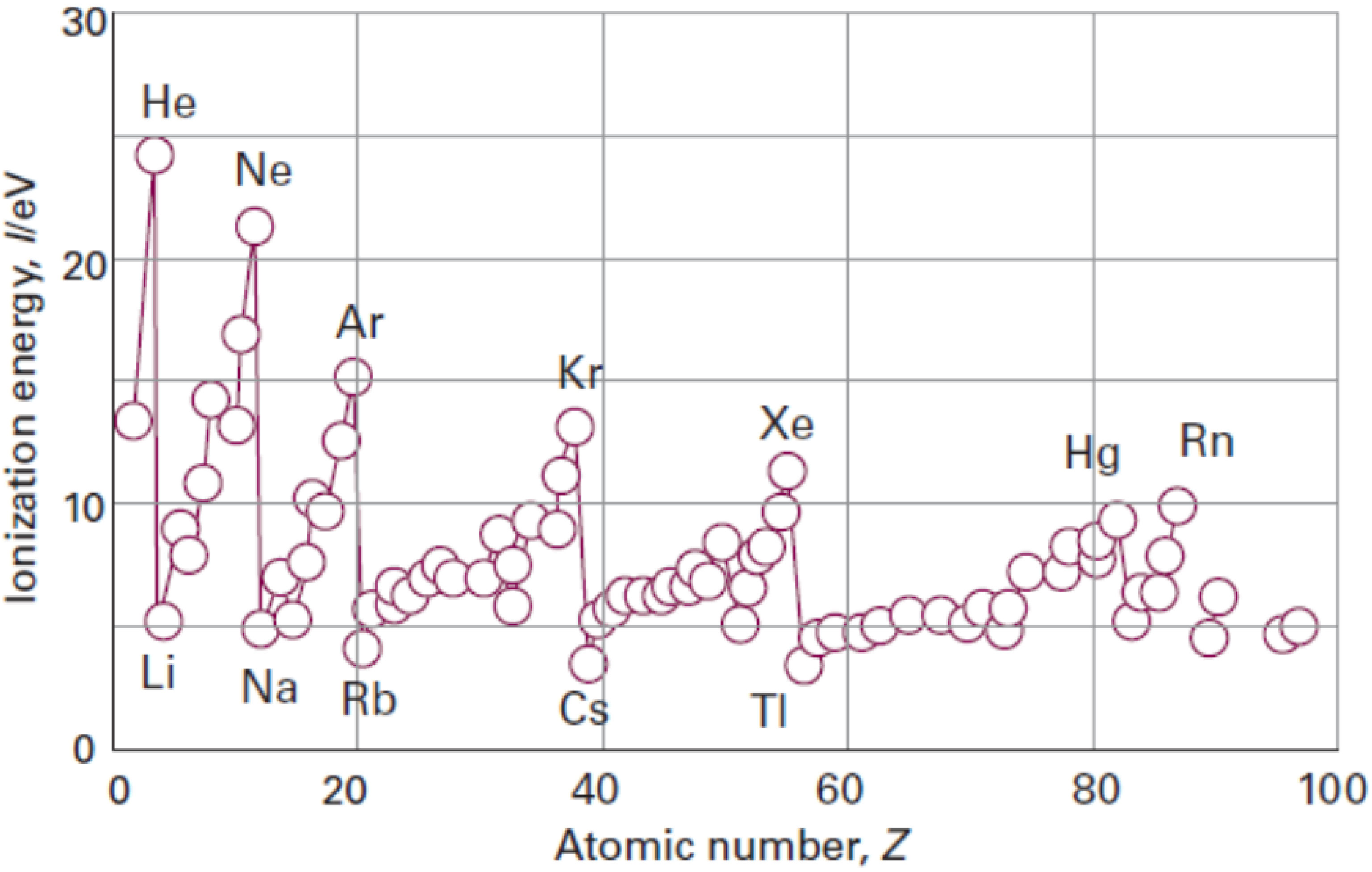
As ionization energy is often easier to measure than electron affinity; this relation can be used to determine numerical values of the latter.

As will be familiar from introductory chemistry, ionization energies and electron affinities show periodicities. The former is more regular and we concentrate on it. Lithium has a low first ionization energy because its outermost electron is well shielded from the nucleus by the core ($Z_{\mathrm{eff}} = 1.3$, compared with $Z = 3$). The ionization energy of beryllium ($Z = 4$) is greater but that of boron is lower than that of beryllium because in the latter the outermost electron occupies a 2p orbital and is less strongly bound than if it had been a 2s electron. The ionization energy increases from boron to nitrogen on account of the increasing nuclear charge. However, the ionization energy of oxygen is less than would be expected by simple extrapolation. The explanation is that at oxygen a 2p orbital must become doubly occupied, and the electron–electron repulsions are increased above what would be expected by simple extrapolation along the row. In addition, the loss of a 2p electron results in a configuration with a half-filled subshell (like that of N), which is an arrangement of low energy, so the energy of $O^+ + e^-$ is lower than might be expected, and the ionization energy is correspondingly low too. (The kink is less pronounced in the next row, between phosphorus and sulfur,

Atomic structure

Ionization energies and electron affinities

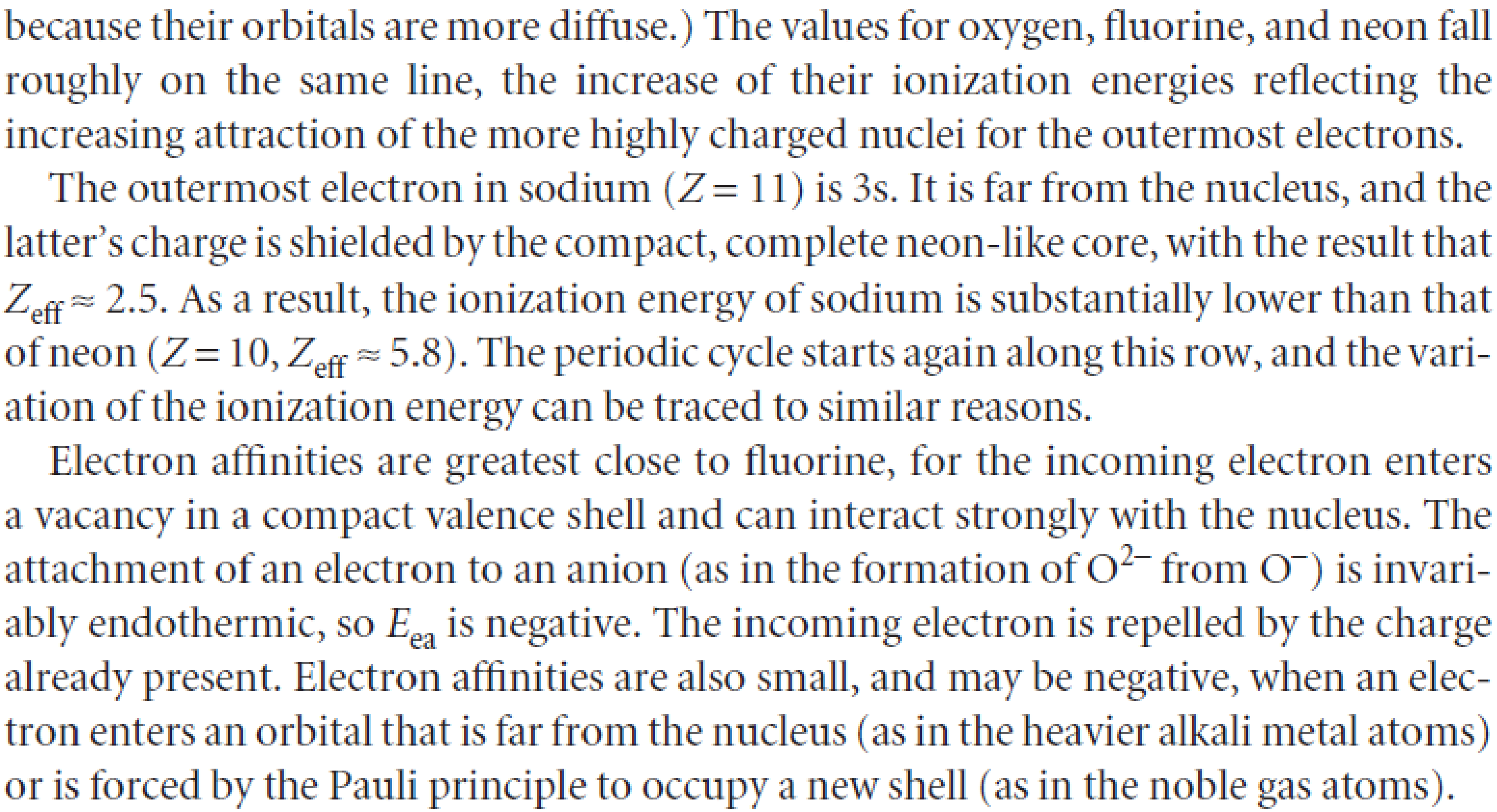
ATOMI A MOLTI ELETTRONI



Atomic structure

Ionization energies and electron affinities

ATOMI A MOLTI ELETTRONI



because their orbitals are more diffuse.) The values for oxygen, fluorine, and neon fall roughly on the same line, the increase of their ionization energies reflecting the increasing attraction of the more highly charged nuclei for the outermost electrons.

The outermost electron in sodium ($Z = 11$) is 3s. It is far from the nucleus, and the latter's charge is shielded by the compact, complete neon-like core, with the result that $Z_{\mathrm{eff}} \approx 2.5$. As a result, the ionization energy of sodium is substantially lower than that of neon ($Z = 10$, $Z_{\mathrm{eff}} \approx 5.8$). The periodic cycle starts again along this row, and the variation of the ionization energy can be traced to similar reasons.

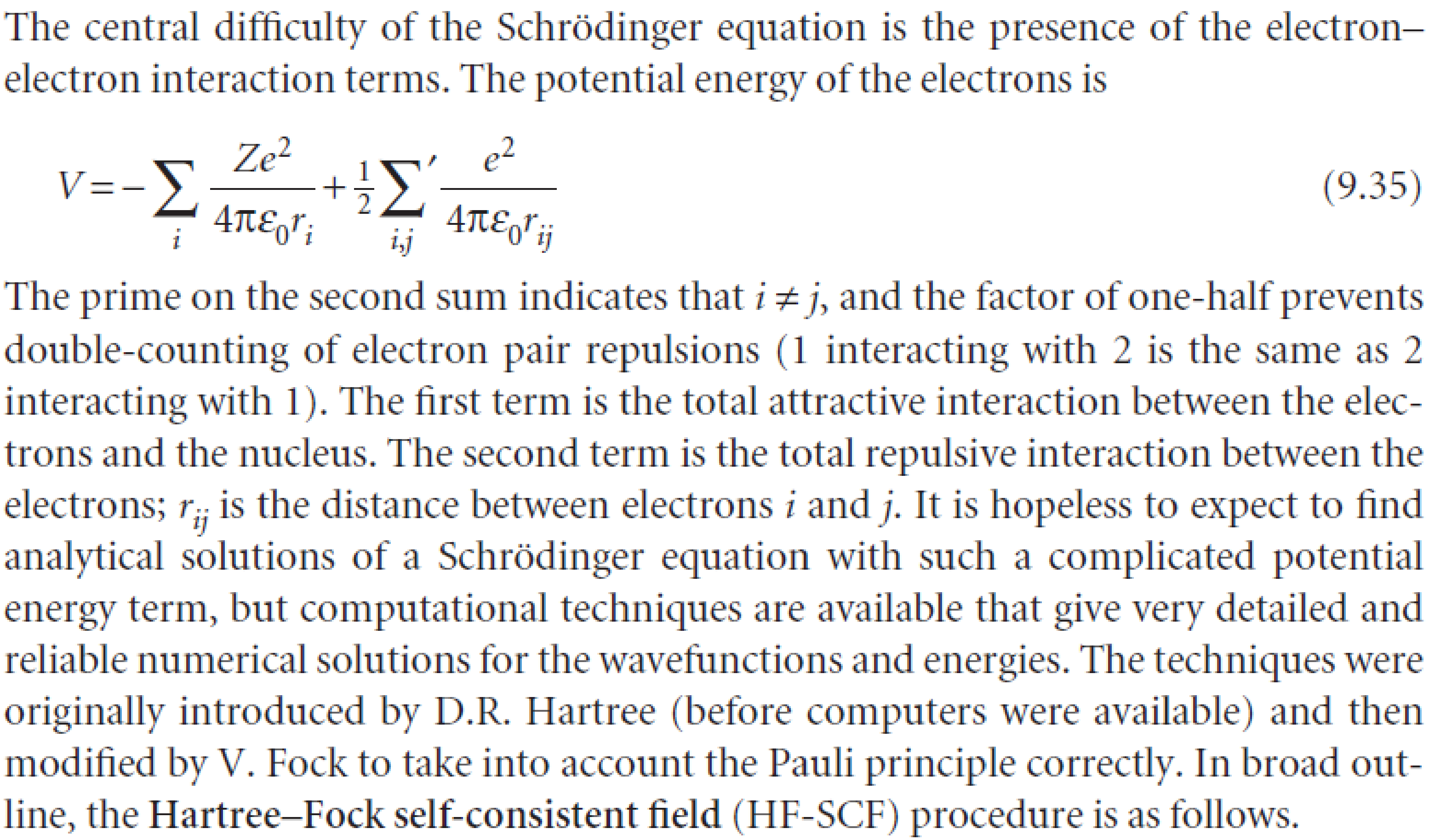
Electron affinities are greatest close to fluorine, for the incoming electron enters a vacancy in a compact valence shell and can interact strongly with the nucleus. The attachment of an electron to an anion (as in the formation of O^{2-} from O^{-}) is invariably endothermic, so E_{ea} is negative. The incoming electron is repelled by the charge already present. Electron affinities are also small, and may be negative, when an electron enters an orbital that is far from the nucleus (as in the heavier alkali metal atoms) or is forced by the Pauli principle to occupy a new shell (as in the noble gas atoms).

Atomic structure

Self-consistent field orbitals

ATOMI A MOLTI ELETTRONI

The Schrödinger equation for many-electron atoms is solved numerically and iteratively until the solutions are self-consistent.



The central difficulty of the Schrödinger equation is the presence of the electron–electron interaction terms. The potential energy of the electrons is

$$V = -\sum_{i} \frac{Ze^2}{4\pi\varepsilon_0 r_i} + \frac{1}{2}\sum_{i,j}{}' \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \qquad (9.35)$$

The prime on the second sum indicates that $i \neq j$, and the factor of one-half prevents double-counting of electron pair repulsions (1 interacting with 2 is the same as 2 interacting with 1). The first term is the total attractive interaction between the electrons and the nucleus. The second term is the total repulsive interaction between the electrons; r_{ij} is the distance between electrons i and j. It is hopeless to expect to find analytical solutions of a Schrödinger equation with such a complicated potential energy term, but computational techniques are available that give very detailed and reliable numerical solutions for the wavefunctions and energies. The techniques were originally introduced by D.R. Hartree (before computers were available) and then modified by V. Fock to take into account the Pauli principle correctly. In broad outline, the **Hartree–Fock self-consistent field** (HF-SCF) procedure is as follows.

Atomic structure

Self-consistent field orbitals

ATOMI A MOLTI ELETTRONI

The Schrödinger equation for many-electron atoms is solved numerically and iteratively until the solutions are self-consistent.

Imagine that we have a rough idea of the structure of the atom. In the Ne atom, for instance, the orbital approximation suggests the configuration $1s^22s^22p^6$ with the orbitals approximated by hydrogenic atomic orbitals. Now consider one of the 2p electrons. A Schrödinger equation can be written for this electron by ascribing to it a potential energy due to the nuclear attraction and the repulsion from the other electrons. This equation has the form

$$\hat{H}(1)\psi_{2p}(1) + V(\text{other electrons})\,\psi_{2p}(1) - V(\text{exchange correction})\,\psi_{2p}(1) = E_{2p}\psi_{2p}(1) \qquad (9.36)$$

Although the equation is for the 2p orbital in neon, it depends on the wavefunctions of all the other occupied orbitals in the atom. A similar equation can be written for the 1s and 2s orbitals in the atom. The various terms are as follows:

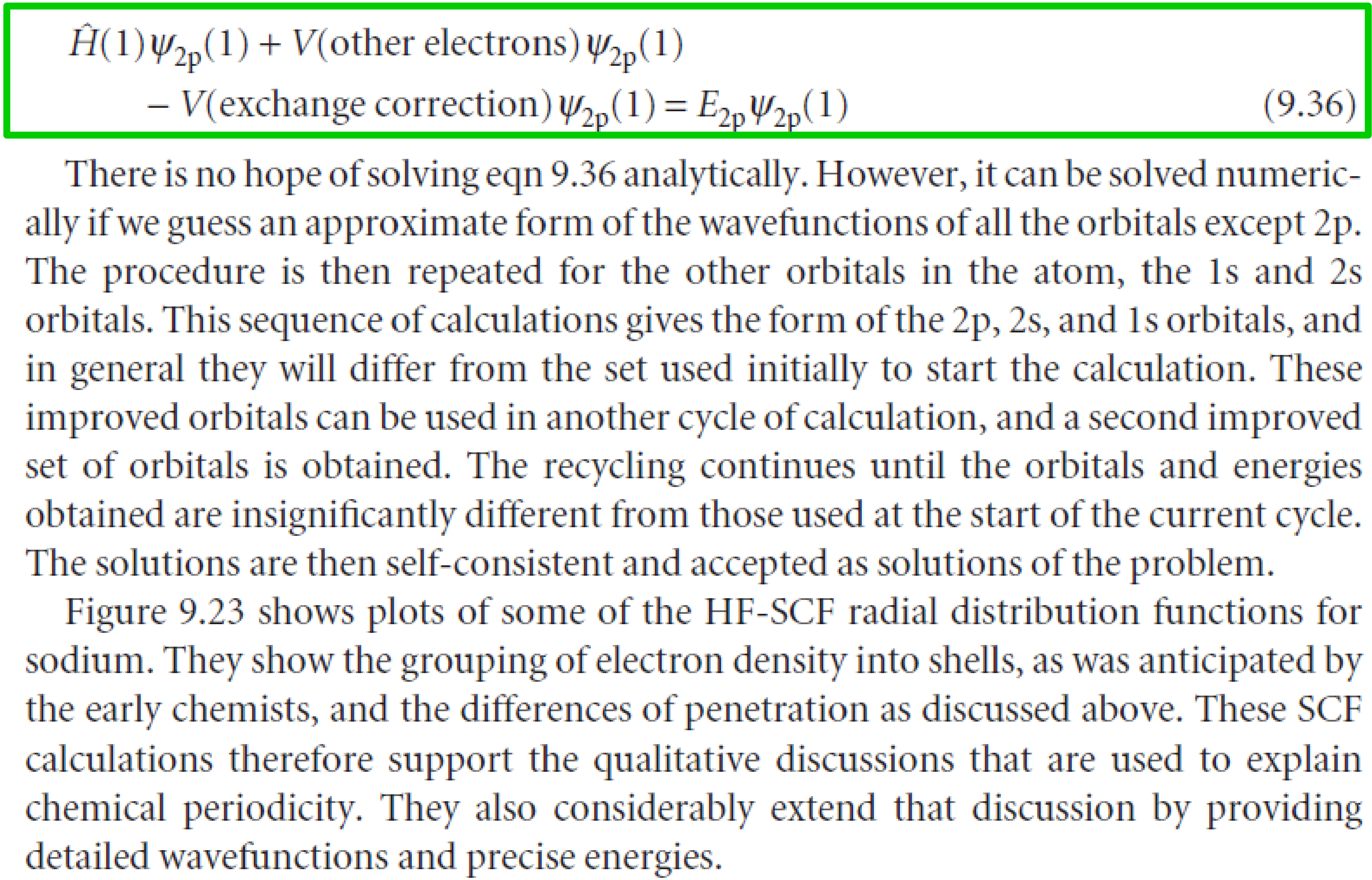
- The first term on the left is the contribution of the kinetic energy and the attraction of the electron to the nucleus, just as in a hydrogenic atom.
- The second term takes into account the potential energy of the electron of interest due to the electrons in the other occupied orbitals.
- The third term is an *exchange correction* that takes into account the spin correlation effects discussed earlier.

Atomic structure

Self-consistent field orbitals

ATOMI A MOLTI ELETTRONI

The Schrödinger equation for many-electron atoms is solved numerically and iteratively until the solutions are self-consistent.



$$\hat{H}(1)\psi_{2p}(1) + V(\text{other electrons})\psi_{2p}(1) - V(\text{exchange correction})\psi_{2p}(1) = E_{2p}\psi_{2p}(1) \qquad (9.36)$$

There is no hope of solving eqn 9.36 analytically. However, it can be solved numerically if we guess an approximate form of the wavefunctions of all the orbitals except 2p. The procedure is then repeated for the other orbitals in the atom, the 1s and 2s orbitals. This sequence of calculations gives the form of the 2p, 2s, and 1s orbitals, and in general they will differ from the set used initially to start the calculation. These improved orbitals can be used in another cycle of calculation, and a second improved set of orbitals is obtained. The recycling continues until the orbitals and energies obtained are insignificantly different from those used at the start of the current cycle. The solutions are then self-consistent and accepted as solutions of the problem.

Figure 9.23 shows plots of some of the HF-SCF radial distribution functions for sodium. They show the grouping of electron density into shells, as was anticipated by the early chemists, and the differences of penetration as discussed above. These SCF calculations therefore support the qualitative discussions that are used to explain chemical periodicity. They also considerably extend that discussion by providing detailed wavefunctions and precise energies.

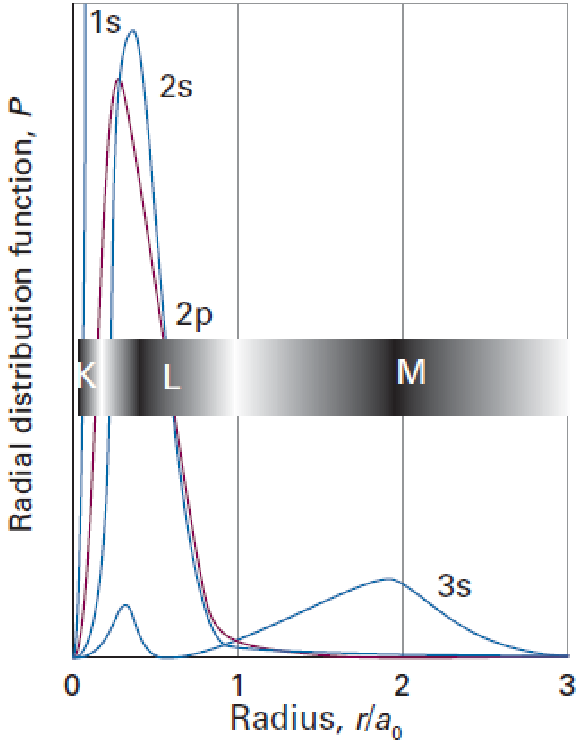
Atomic structure

Self-consistent field orbitals

ATOMI A MOLTI ELETTRONI

The Schrödinger equation for many-electron atoms is solved numerically and iteratively until the solutions are self-consistent.

Figure 9.23 shows plots of some of the HF-SCF radial distribution functions for sodium. They show the grouping of electron density into shells, as was anticipated by the early chemists, and the differences of penetration as discussed above. These SCF calculations therefore support the qualitative discussions that are used to explain chemical periodicity. They also considerably extend that discussion by providing detailed wavefunctions and precise energies.



Atomic structure

Self-consistent field orbitals

Studiamo solo lo schema di accoppiamento di Russel-Saunders.

COSA GLI STUDENTI DEVONO ESSERE IN GRADO DI FARE CON I TERMINI SPETTROSCOPICI

- **Saper contare il numero di microstate rappresentati da una certa CONFIGURAZIONE ELETTRONICA.**

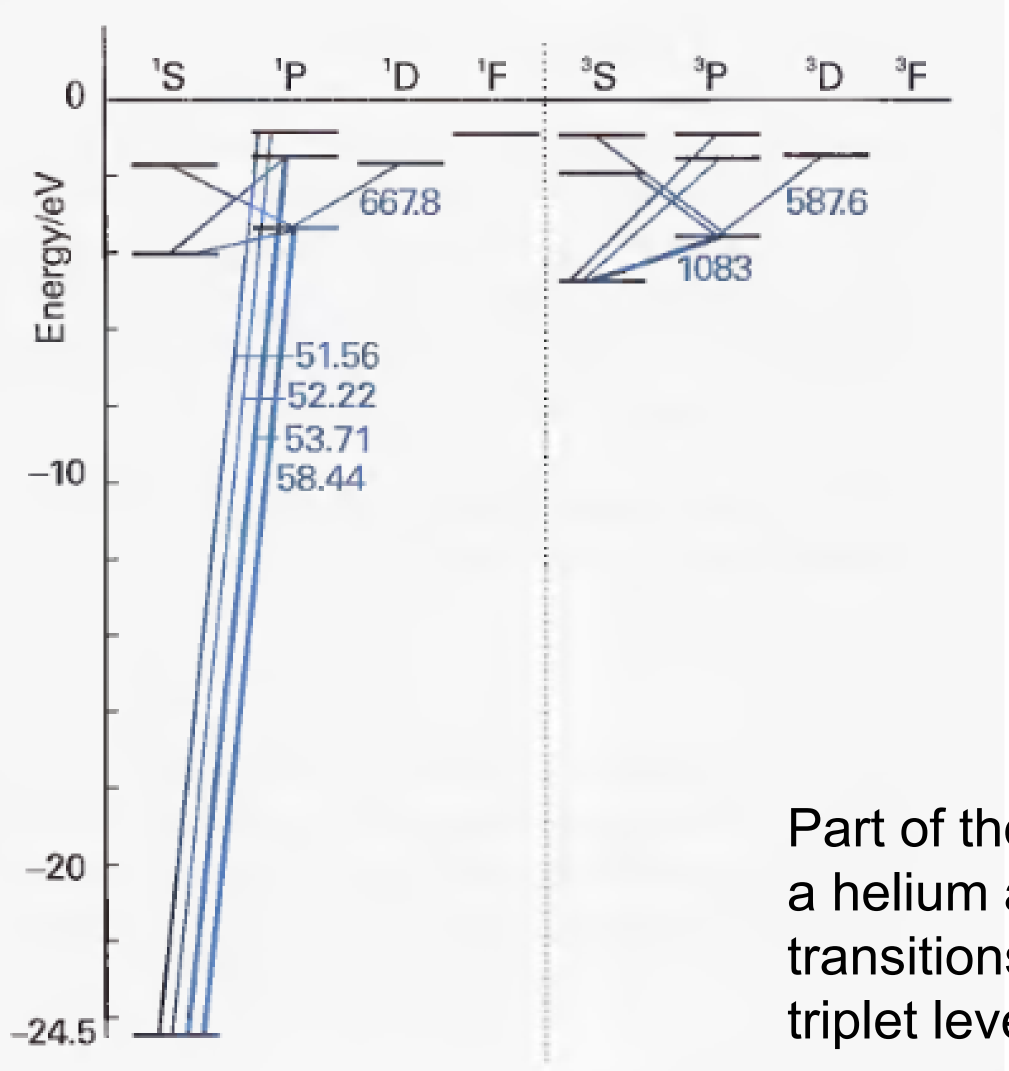
- **Conoscere il significato della notazione (del tipo $^2P_{3/2}$) e saper associare i corretti valori dei numeri quantici L, S, J ai termini spettroscopici.**

- **Saper prevedere il termine spettroscopico per configurazioni elettroniche semplici in cui non ci sono TERMINI eliminate dal principio di esclusione di Pauli.**

- **Conoscere le regole di selezione per atomi a molti elettroni: quali sono e che cosa significano.**

Atomic structure

The structures of many-electron atoms



He :

Stato fondamentale $1s^2$

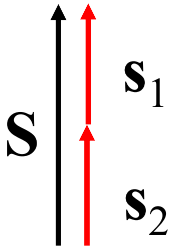
Uno degli stati eccitati $1s^1\,2s^1$

Part of the Grotrian diagram for a helium atom. Note that there are no transitions between the singlet and triplet levels.

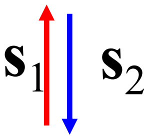
Atomic structure The structures of many-electron atoms

Singlet and triplet states

La combinazione degli spin di due elettroni avviene secondo le regole della meccanica quantistica (i simboli in grassetto indicano vettori)



$\mathbf{S} \neq \mathbf{0}$



$\mathbf{S} = \mathbf{0}$

In ogni caso valgono le relazioni $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$

$$S_z = s_{z1} + s_{z2}$$

Le funzioni di spin per due elettroni sono autofunzioni degli operatori dello spin totale $\hat{S}^2$ e $\hat{S}_z$ definiti come segue

$$\hat{S}^2 = (\hat{\mathbf{S}})^2 = (\hat{\mathbf{s}}_1 + \hat{\mathbf{s}}_2)^2 = \hat{s}_1{}^2 + \hat{s}_2{}^2 + 2\,\hat{\mathbf{s}}_1 \cdot \hat{\mathbf{s}}_2$$
$$\hat{S}_z = \hat{s}_{z1} + \hat{s}_{z2}$$

Atomic structure The structures of many-electron atoms

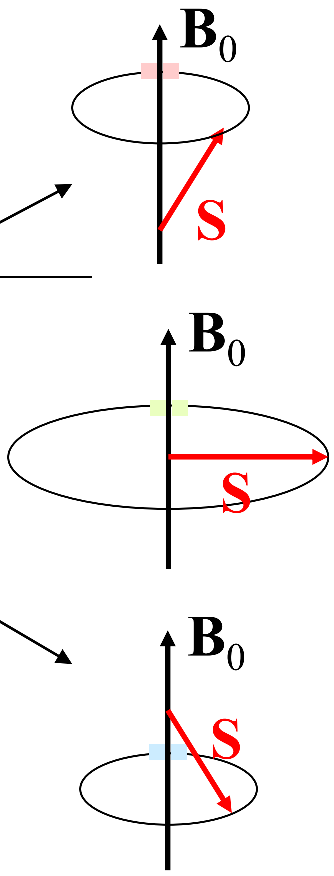
Singlet and triplet states

$\hat{S}^2\ \phi = S(S+1)\ \phi$

$\hat{S}_z\ \phi = M_S\ \phi$

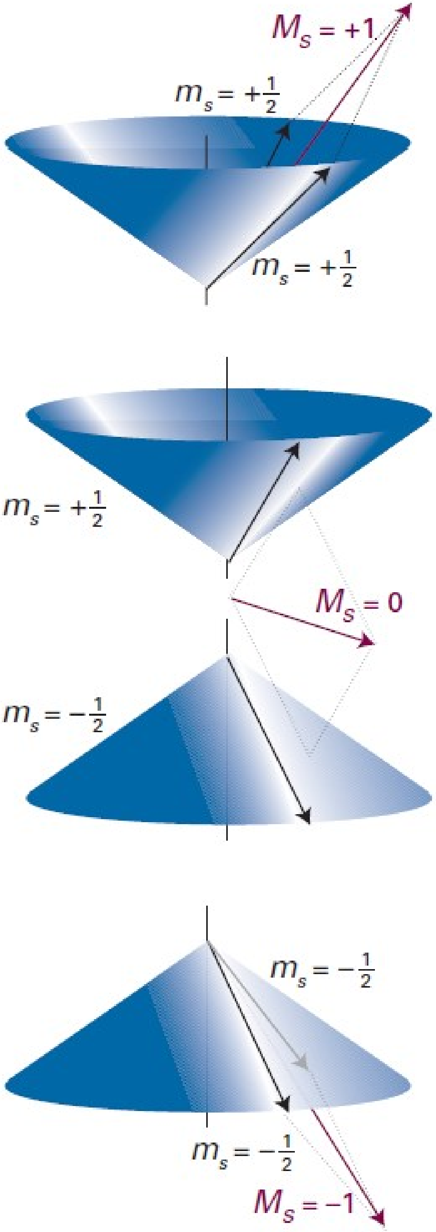
numeri quantici

		ϕ	S	S(S+1)	M_S
tripletto	τ_1	$\alpha(1)\alpha(2) = \alpha\alpha$	1	2	+1
	σ_+	$1/\sqrt{2}\ \{ \alpha\beta + \beta\alpha \}$	1	2	0
	τ_{-1}	$\beta\beta$	1	2	-1
singoletto	σ_-	$1/\sqrt{2}\ \{ \alpha\beta - \beta\alpha \}$	0	0	0



Atomic structure

The structures of many-electron atoms



triplet state

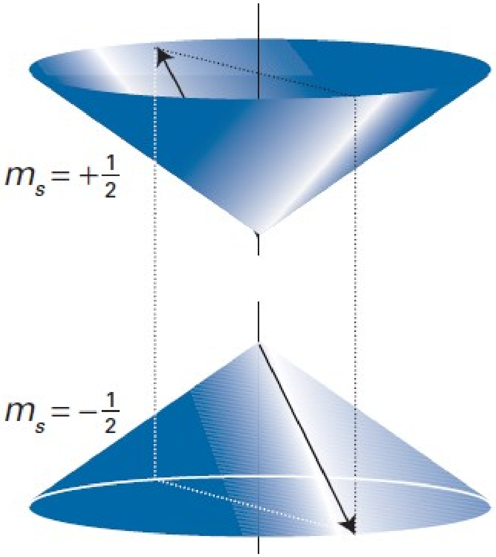
When two electrons have parallel spins, they have a nonzero total spin angular momentum. There are three ways of achieving this resultant, which are shown by these vector representations.

Note that, although we cannot know the orientation of the spin vectors on the cones, the angle between the vectors is the same in all three cases, for all three arrangements have the same total spin angular momentum (that is, the resultant of the two vectors has the same length in each case, but points in different directions). Compare this diagram with Fig. 9.18, which shows the antiparallel case. Note that, whereas two paired spins are precisely antiparallel, two 'parallel' spins are not strictly parallel.

Atomic structure

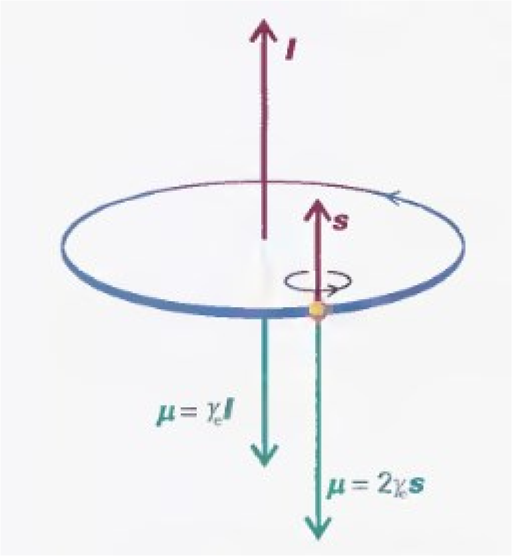
The structures of many-electron atoms

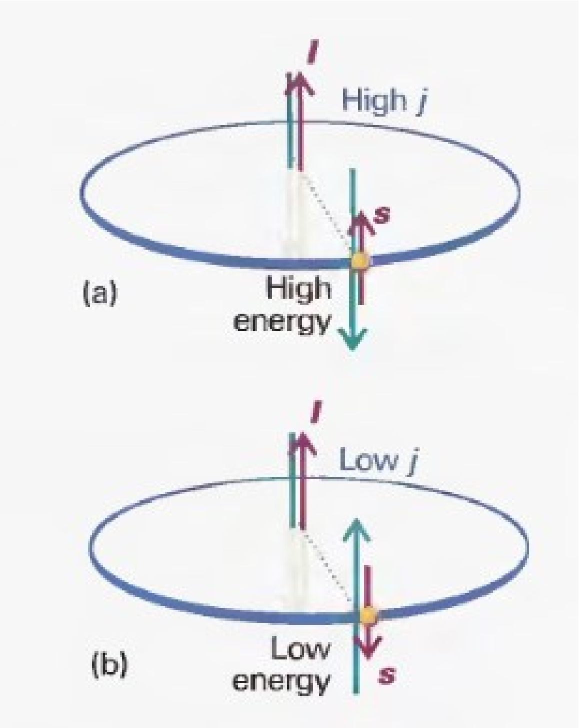
Singlet state



Electrons with paired spins have zero resultant spin angular momentum.
They can be represented by two vectors that lie at an indeterminate position on the cones shown here, but, wherever one lies on its cone, the other points in the opposite direction; their resultant is zero.

Spin-orbit coupling





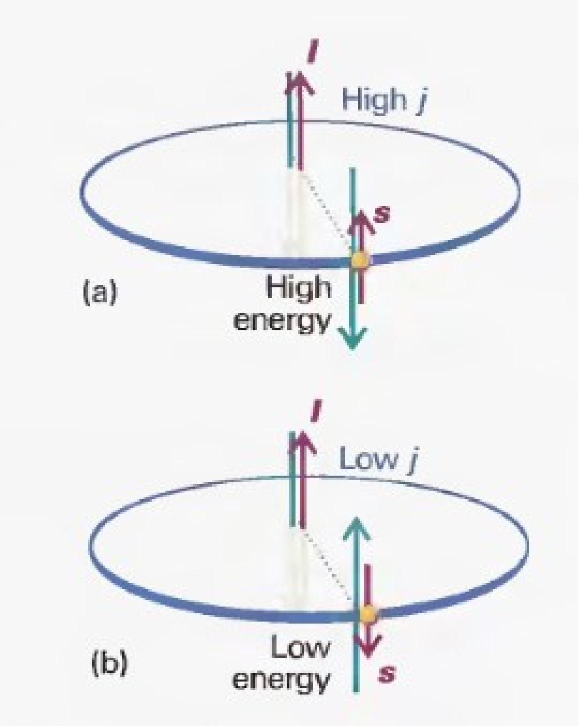
Angular momentum gives rise to a magnetic moment (μ). For an electron, the magnetic moment is antiparallel to the orbital angular momentum, but proportional to it. For spin angular momentum, there is a factor 2, which increases the magnetic moment to twice its expected value.

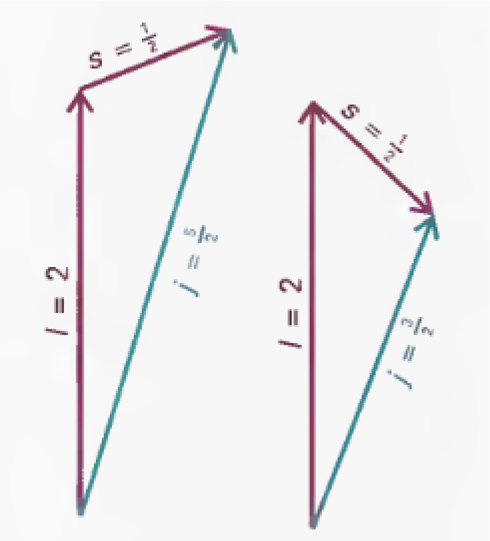
Spin-orbit coupling is a magnetic interaction between spin and orbital magnetic moments. When the angular momenta are parallel, as in (a), the magnetic moments are aligned unfavourably; when they are opposed, as in (b), the interaction is favourable. This magnetic coupling is the cause of the splitting of a configuration into levels.

Atomic structure

The structures of many-electron atoms

Spin-orbit coupling



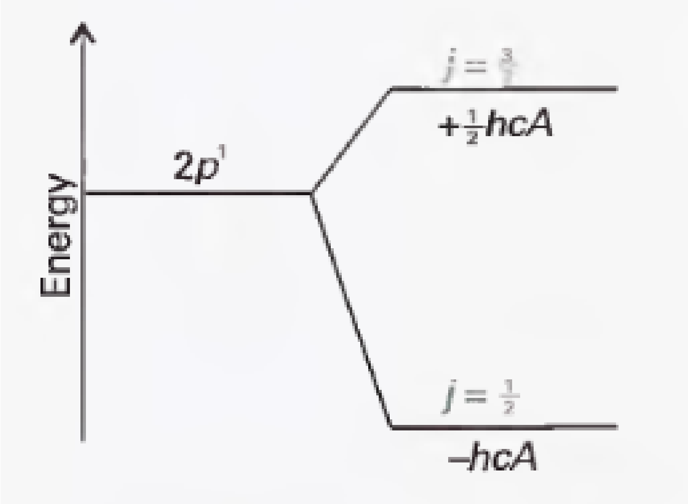


The coupling of the spin and orbital angular momenta of a d electron (*l* = 2) gives two possible values of *j* depending on the relative orientations of the spin and orbital angular momenta of the electron.

Spin-orbit coupling

Metallo alcalino (Li, Na, K, …) :

Stato fondamentale **[g.n.] ns^1**
Uno degli stati eccitati **[g.n.] np^1**

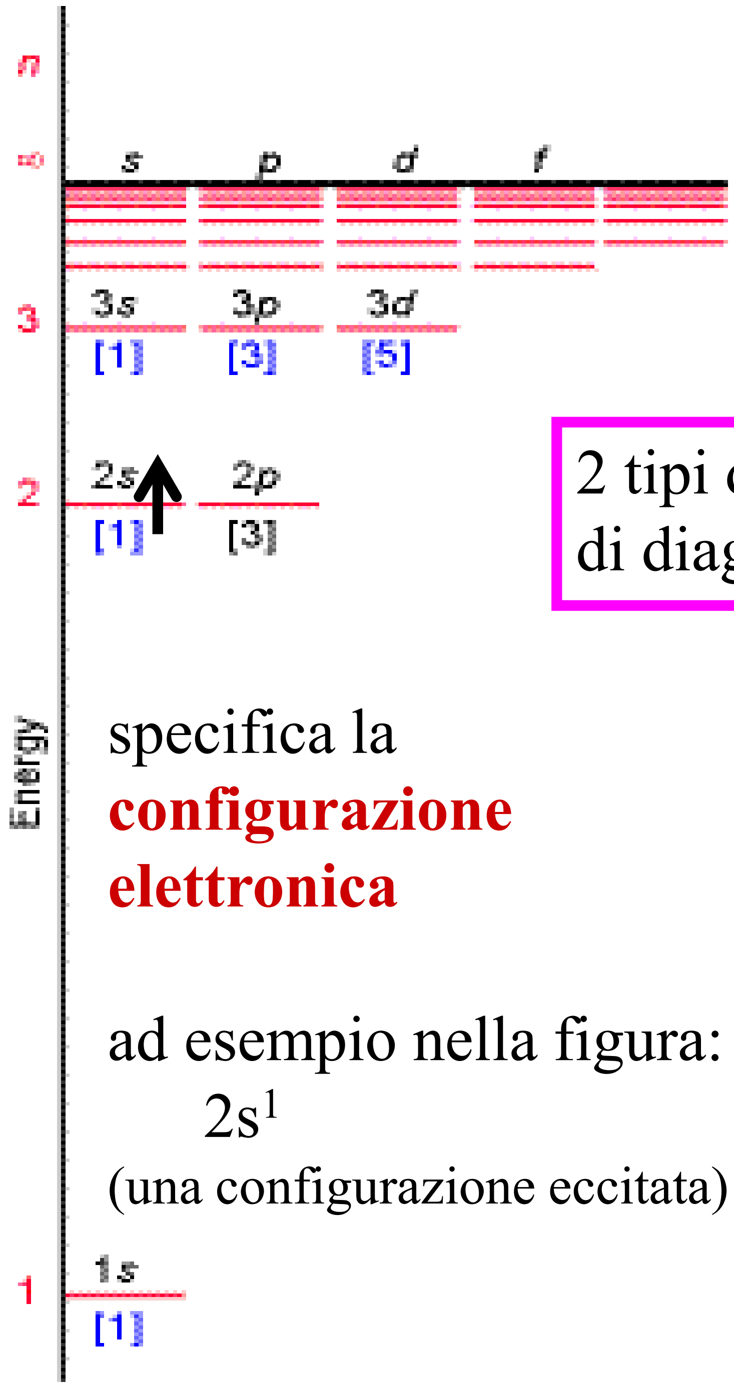


$$E_{l,s,j} = \tfrac{1}{2}hcA\{j(j+1) - l(l+1) - s(s+1)\}$$

$$E_{3/2} = \tfrac{1}{2}hcA\{\tfrac{3}{2} \times \tfrac{5}{2} - 1 \times 2 - \tfrac{1}{2} \times \tfrac{3}{2}\} = \tfrac{1}{2}hcA$$
$$E_{1/2} = \tfrac{1}{2}hcA\{\tfrac{1}{2} \times \tfrac{3}{2} - 1 \times 2 - \tfrac{1}{2} \times \tfrac{3}{2}\} = -hcA$$

The levels of a ^2P term arising from spin-orbit coupling. Note that the low-j level lies below the high-j level in energy.

Diagramma di Grotrian per l'atomo di sodio



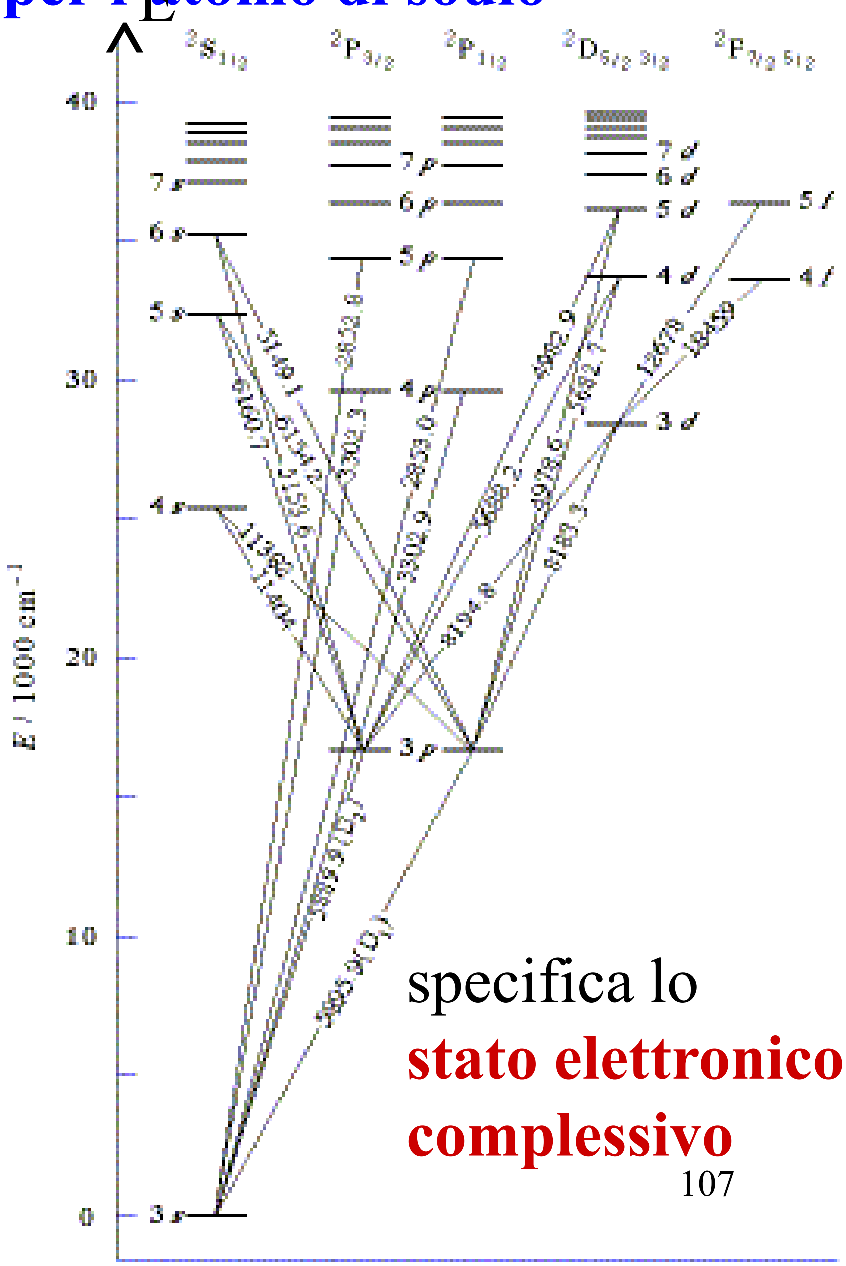
2 tipi diversi di diagrammi

specifica la **configurazione elettronica**

ad esempio nella figura:

$2s^1$

(una configurazione eccitata)



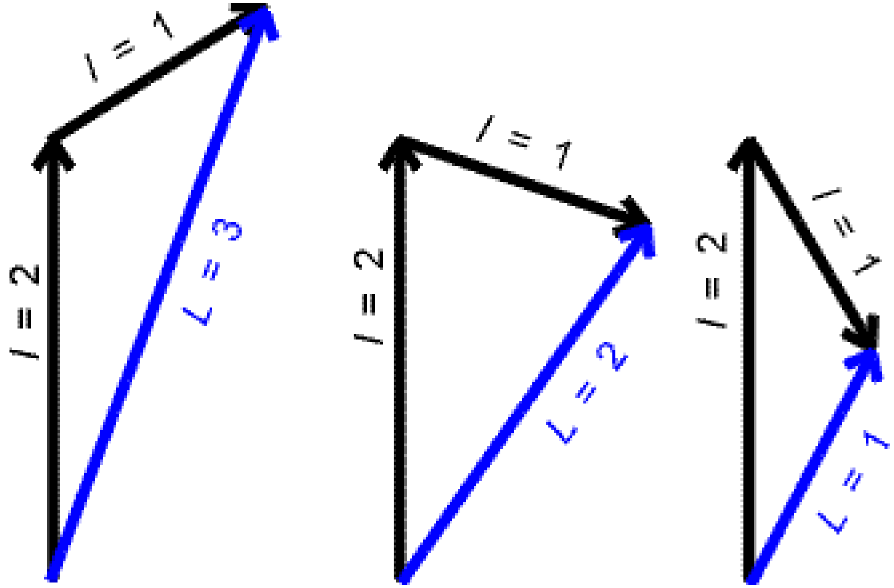
specifica lo **stato elettronico complessivo**

Atomi a 2 o più elettroni

Momento angolare orbitale TOTALE $\vec{L}$ per atomi a 2 o più elettroni

$$\vec{L} = \sum_i \vec{\ell}_i \qquad L_z = \sum_i \ell_{zi} = M_L \hbar = \sum_i m_{\ell i} \hbar$$

$$\left|\vec{L}\right|^2 = ?$$



Diversi possibili modi di sommarsi di 2 momenti angolari con numeri quantici ℓ_1=2 e ℓ_2 =1 per dare il **momento angolare totale** con numero quantico L = 3, 2, 1.

$$L = l_1 + l_2, l_1 + l_2 - 1, \ldots, |l_1 - l_2|$$ **METODO GENERALE**

Il numero quantico L può avere solo valori interi ≥ 0

Atomi a 2 o più elettroni

Momento angolare orbitale TOTALE $\vec{L}$ per atomi a 2 o più elettroni

L:	0	1	2	3	4	5	6
	S	P	D	F	G	H	I

Atomi a 2 o più elettroni

Momento angolare di spin TOTALE $\vec{S}$ per atomi a 2 o più elettroni

$$\vec{S} = \sum_i \vec{s}_i \qquad S_z = \sum_i s_{zi} = M_S \hbar = \sum_i m_{si} \hbar$$

$$\left|\vec{S}\right|^2 = ?$$

numero quantico S del vettore somma $\vec{S}$

$S = s_1 + s_2 , s_1 + s_2 - 1, \dots , | s_1 - s_2 |$ **METODO GENERALE**

Struttura Atomica

Atomi a 2 o più elettroni

Momento angolare orbitale TOTALE $\vec{L}$ $\left|\vec{\boldsymbol{L}}\right|^2 = ?$

Momento angolare di spin TOTALE $\vec{S}$ $\left|\vec{S}\right|^2 = ?$

Gli stati possibili vengono raggruppati in modo da avere lo stesso valore
del numero quantico S,
del numero quantico L
e del numero quantico J

Termini spettroscopici $^{2S+1}T_J$

Atomi a 2 o più elettroni

Termini spettroscopici

$$^{2S+1}T_J$$

2S+1 = molteplicità di spin

T può essere S, P, D, F, ……

J è il numero quantico del momento angolare totale (moto orbitale + spin)

$$J=L+S\ ,\ \ L+S-1\ ,\ \ L+S-2,\ \ \ldots\ \ ,\ \ |\,L-S\,|$$

Struttura Atomica

S=1/2 L=0
J=1/2

$^2S_{1/2}$

S=1/2 L=1
J=3/2

$^2P_{3/2}$

S=1/2 L=1
J=1/2

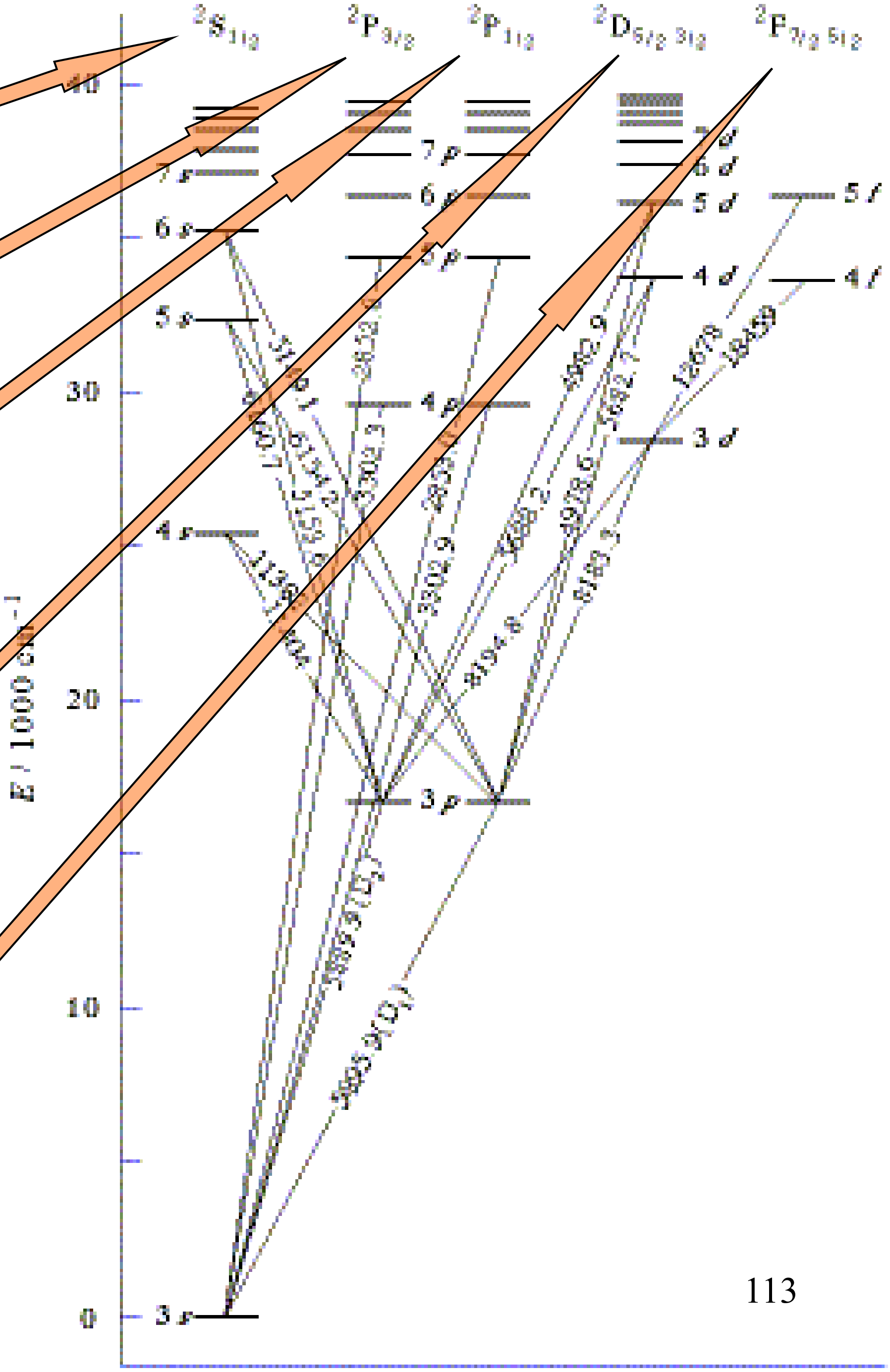
$^2P_{1/2}$

S=1/2 L=2
J=5/2 e 3/2

$^2D_{5/2}$ $^2D_{3/2}$

S=1/2 L=3
J=7/2 e 5/2

$^2F_{7/2}$ $^2F_{5/2}$



Selection rules

$$\boldsymbol{\mu}_{\mathrm{fi}} = -e\int \psi_{\mathrm{f}}^{*}\,\boldsymbol{r}\,\psi_{\mathrm{i}}\,\mathrm{d}\tau$$

For a one-electron atom μ is multiplication by -*er* with components μ_x = -*ex*, μ_y = - *ey*, and μ_z = - *ez*. If the transition dipole moment is zero, the transition is forbidden; the transition is allowed if the transition moment is non-zero.

$$\Delta L = 0\ ,\ \pm 1$$
$$\Delta \ell = \pm 1$$
$$\Delta S = 0$$
$$\Delta J = 0\ ,\ \pm 1$$

ma $J=0 \leftrightarrow J=0$ è proibita

$$\mu_{z,\mathrm{fi}} = -e\int \psi_{\mathrm{f}}^{*}\,z\,\psi_{\mathrm{i}}\,\mathrm{d}\tau$$

And similar expressions for μ_y and μ_z