

Átomos multielectrónicos

En la aproximación de partículas independientes.

$$H = H_c + H_1 \quad \leftarrow \text{perturbación}$$

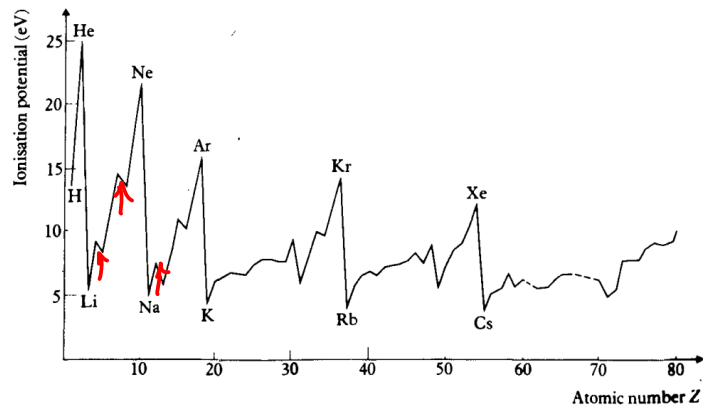
$$H_c = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_{r_i}^2 + V(r_i) \right) \quad H_1 = \sum_{i < j=1}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \left(\frac{Z}{r_i} + V(r_i) \right)$$

A orden cero

$$E_c = \sum_{i=1}^N E_{n_i l_i} \Rightarrow \{n_1 l_1, n_2 l_2, \dots, n_N l_N\}$$

Table 7.2 Electronic configuration, term value and ionisation potential of the atoms in their ground state

Z	Element	Electronic configuration†	Subcapa	Term†	Capa	Ionisation potential (eV)
1	H hydrogen	1s		$^2S_{1/2}$		13.60
2	He helium	1s ²		1S_0	1	24.59
3	Li lithium	[He]2s	s	$^2S_{1/2}$	2	5.39
4	Be beryllium	[He]2s ²		1S_0		9.32
5	B boron	[He]2s ² 2p	p	$^2P_{1/2}$	2	8.30
6	C carbon	[He]2s ² 2p ²		3P_0		11.26
7	N nitrogen	[He]2s ² 2p ³		$^4S_{3/2}$		14.53
8	O oxygen	[He]2s ² 2p ⁴		3P_2		13.62
9	F fluorine	[He]2s ² 2p ⁵	$^2P_{3/2}$	17.42		
10	Ne neon	[He]2s ² 2p ⁶	1S_0	21.56		
11	Na sodium	[Ne]3s		$^2S_{1/2}$		5.14
12	Mg magnesium	[Ne]3s ²		1S_0	1	7.65
13	Al aluminium	[Ne]3s ² 3p	p	$^2P_{1/2}$	3	5.99
14	Si silicon	[Ne]3s ² 3p ²		3P_0		8.15
15	P phosphorus	[Ne]3s ² 3p ³		$^4S_{3/2}$		10.49
16	S sulphur	[Ne]3s ² 3p ⁴		3P_2		10.36
17	Cl chlorine	[Ne]3s ² 3p ⁵	$^2P_{1/2}$	12.97		
18	Ar argon	[Ne]3s ² 3p ⁶	1S_0	15.76		
19	K potassium	[Ar]4s		$^2S_{1/2}$		4.34
20	Ca calcium	[Ar]4s ²		1S_0	1	6.11
21	Sc scandium	[Ar]4s ² 3d	d	$^2D_{3/2}$	4	6.54
22	Ti titanium	[Ar]4s ² 3d ²		3F_2		6.82
23	V vanadium	[Ar]4s ² 3d ³		$^4F_{3/2}$		6.74
24	Cr chromium	[Ar]4s ¹ 3d ⁵		7S_3		6.77
25	Mn manganese	[Ar]4s ² 3d ⁵	$^6S_{5/2}$	7.44		
26	Fe iron	[Ar]4s ² 3d ⁶	5D_4	7.87		
27	Co cobalt	[Ar]4s ² 3d ⁷	$^4F_{9/2}$	7.86		
28	Ni nickel	[Ar]4s ² 3d ⁸	3F_4	7.64		
29	Cu copper	[Ar]4s ¹ 3d ¹⁰	$^2S_{1/2}$	7.73		
30	Zn zinc	[Ar]4s ² 3d ¹⁰	1S_0	9.39		
31	Ga gallium	[Ar]4s ² 3d ¹⁰ 4p		$^2P_{1/2}$		6.00
32	Ge germanium	[Ar]4s ² 3d ¹⁰ 4p ²		3P_0	1	7.90
33	As arsenic	[Ar]4s ² 3d ¹⁰ 4p ³		$^4S_{3/2}$	2	9.81
34	Se selenium	[Ar]4s ² 3d ¹⁰ 4p ⁴		3P_2	3	9.75
35	Br bromine	[Ar]4s ² 3d ¹⁰ 4p ⁵		$^2P_{1/2}$	4	11.81
36	Kr krypton	[Ar]4s ² 3d ¹⁰ 4p ⁶		1S_0	5	14.00
37	Rb rubidium	[Kr]5s		$^2S_{1/2}$		4.18
38	Sr strontium	[Kr]5s ²		1S_0	1	5.70
39	Y yttrium	[Kr]5s ² 4d	d	$^2D_{3/2}$	6	6.38
40	Zr zirconium	[Kr]5s ² 4d ²		3F_2		6.84
41	Nb niobium	[Kr]5s ² 4d ³		$^6D_{1/2}$		6.88
42	Mo molybdenum	[Kr]5s ¹ 4d ⁵		7S_3		7.10
43	Tc technetium	[Kr]5s ² 4d ⁵	$^6S_{5/2}$	7.28		
44	Ru ruthenium	[Kr]5s ² 4d ⁶	5F_4	7.37		
45	Rh rhodium	[Kr]5s ² 4d ⁷	$^4F_{9/2}$	7.46		
46	Pd palladium	[Kr]4d ¹⁰		1S_0	1	8.34
47	Ag silver	[Kr]5s ¹ 4d ¹⁰		$^2S_{1/2}$	2	7.58
48	Cd cadmium	[Kr]5s ² 4d ¹⁰		1S_0	3	8.99
49	In indium	[Kr]5s ² 4d ¹⁰ 5p		$^2P_{1/2}$	4	5.79
50	Sn tin	[Kr]5s ² 4d ¹⁰ 5p ²		3P_0	5	7.34
51	Sb antimony	[Kr]5s ² 4d ¹⁰ 5p ³		$^4S_{3/2}$	6	8.64



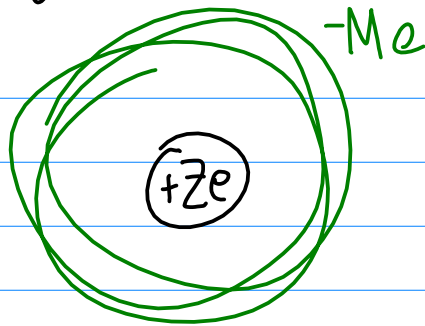
7.1 The ionisation potential as a function of the atomic number Z. The maxima occur at Z = 2 (He), Z = 10 (Ne), Z = 18 (Ar), Z = 36 (Kr), Z = 54 (Xe) and (not shown) Z = 86 (Rn).

n común capa
(n-1) común subcapa

Elemento de gas noble:
Cuando la subcapa p se llena y helio.

Electrones en la misma subcapa tienen la misma distribución espacial y no apantallan al núcleo.

Apantallamiento



$$e^-$$
$$-\frac{(Z-M)e^2}{4\pi\epsilon_0 r}$$

• Método de Thomas-Fermi

- Puede obtener $V(r)$

- Usa modelo de gas de e^- no interactuante

- No da resultados cuantitativos.

- Precursor de DFT (density functional theory)

• Método de Hartree-Fock (método de campo autoconsistente)

Usa determinantes de Slater.

$$\Psi(r_1, \dots, r_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_\alpha(r_1) & u_\beta(r_1) & \dots & u_\nu(r_1) \\ \vdots & \vdots & & \vdots \\ u_\alpha(r_N) & u_\beta(r_N) & \dots & u_\nu(r_N) \end{vmatrix}$$

normalización \rightarrow

ocupan orbitales $u_\alpha, u_\beta, \dots, u_\nu$
 \uparrow
conjunto de # cuánticos

Antisimétrico por construcción

- $r_i \leftrightarrow r_j$ cambia el signo
- es cero si dos filas se repiten (si dos conjuntos de números cuánticos se repiten)

Hartree - Fock

- Usar método variacional
- Determinante de Slater como función de prueba.

Si nos enfocamos en el ed. base

$$E_0 \leq E[|\phi\rangle] = \langle \phi | H | \phi \rangle$$

$$|\phi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} |\alpha\rangle_1 & \dots & |\nu\rangle_1 \\ \vdots & & \vdots \\ |\alpha\rangle_N & \dots & |\nu\rangle_N \end{vmatrix}$$

estado partícula

Usaremos

$$\langle \mu | \lambda \rangle = \delta_{\mu\lambda}$$

$$|\phi\rangle = \frac{1}{\sqrt{N!}} \sum_{P \in \mathcal{P}_N} (-1)^{P} P |\alpha\rangle_1 |\beta\rangle_2 \dots |\nu\rangle_N$$

permutación

Paridad de permutación
todas las permutaciones

función de onda de Hartree



$$|\phi\rangle = \sqrt{N!} \mathcal{A} |\phi_H\rangle$$

con $|\phi_H\rangle = |\alpha\rangle_1 |\beta\rangle_2 \dots |\nu\rangle_N$

Operador de antisimetrización
(o antisimetrizador)

$$\mathcal{A} = \frac{1}{N!} \sum_P (-1)^P P$$

Propiedades

$$\mathcal{A}^2 = \mathcal{A}$$

$$\mathcal{A} [12] = \frac{1}{2} ([12] - [21])$$

↓ si hacemos el cambio 2 → 1

$$\frac{1}{2} ([21] - [12]) = -\frac{1}{2} ([12] - [21])$$

$$\begin{aligned} \mathcal{A}^2 ([12] - [21]) &= \frac{1}{4} ([12] - [21] - [21] + [12]) \\ &= \frac{1}{2} ([12] - [21]) \end{aligned}$$

$$\mathcal{A}^\dagger = \mathcal{A}$$

$$\text{Además } [H_1, \mathcal{A}] = [H_2, \mathcal{A}] = 0$$

$$\text{Con } H = H_1 + H_2 ; \quad H_1 = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) = \sum_{i=1}^N h_i$$

$$H_2 = \sum_{i < j=1}^N \frac{1}{r_{ij}} \quad r_{ij} = |\vec{r}_i - \vec{r}_j|$$

Ya tenemos los elementos para escribir el funcional de energía

$$E[|\phi\rangle] = \langle \phi | H_1 | \phi \rangle + \langle \phi | H_2 | \phi \rangle$$

con $\langle \phi | \phi \rangle = 1$ $|\phi\rangle$ es determinante de Slater

Vamos por partes

$$\langle \phi | H_1 | \phi \rangle = N! \langle \phi_H | \mathcal{A} H_1 \mathcal{A} | \phi_H \rangle$$

$$= N! \langle \phi_H | H_1 \mathcal{A}^2 | \phi_H \rangle$$

$$= N! \langle \phi_H | H_1 | \phi_H \rangle$$

$$= \sum_i \sum_p (-1)^p \langle \phi_H | h_i P | \phi_H \rangle$$

hay tantos orbitales como partículas (*)

$$h = -\frac{1}{2} \nabla^2 - \frac{Z}{r}$$

$$= \sum_i \langle \phi_H | h_i | \phi_H \rangle$$

$$= \sum_{\lambda} \langle \lambda | h | \lambda \rangle = \sum_{\lambda} I_{\lambda}$$

Sin P

$$\langle \nu | \dots \langle \lambda | \dots \langle \beta | \langle \alpha | h_i | \alpha \rangle | \beta \rangle \dots | \lambda \rangle \dots | \nu \rangle_N = \langle \lambda | h_i | \lambda \rangle \delta_{\alpha\alpha} \dots \delta_{\nu\nu}$$

↑
Sin $\delta_{\lambda\lambda}$

Con una permutacion P_{jk}

$$\langle \nu | \dots \langle \mu | \langle \lambda | \dots \langle \beta | \langle \alpha | h_i P_{jk} | \alpha \rangle | \beta \rangle \dots | \lambda \rangle | \mu \rangle \dots | \nu \rangle_N = \langle \lambda | h_i | \mu \rangle \delta_{\alpha\alpha} \dots \delta_{\nu\nu}$$

↑
 $\delta_{\mu\lambda}$

Con permutacion P_{ij}

$$\langle \nu | \dots \langle \mu | \langle \lambda | \dots \langle \beta | \langle \alpha | h_i P_{ij} | \alpha \rangle | \beta \rangle \dots | \lambda \rangle | \mu \rangle \dots | \nu \rangle_N = \langle \lambda | h_i | \mu \rangle \delta_{\alpha\alpha} \dots \delta_{\nu\nu}$$

↑
 $\delta_{\lambda\mu}$

Si hay permutacion no deje todo igual, el termino se anula.

Para $\langle \phi | H_2 | \phi \rangle$ es similar

$$\langle \phi | H_2 | \phi \rangle = \sum_{i,j=1}^N \sum_p (-1)^p \langle \phi_H | \frac{1}{r_{ij}} P | \phi_H \rangle$$

$${}_N \langle \nu | \dots | \mu | \langle \lambda | \dots \langle \alpha | \frac{1}{r_{ij}} P_{1N} | \alpha \rangle_1 \dots | \lambda \rangle_i | \mu \rangle_j \dots | \nu \rangle_N = \langle \mu | \langle \lambda | \frac{1}{r_{ij}} | \lambda \rangle_i | \mu \rangle_j \delta_{\alpha\mu} \delta_{\nu\mu} \dots$$

(hacemos un espectro por simplicidad)

$${}_N \langle \nu | \dots | \mu | \langle \lambda | \dots \langle \alpha | \frac{1}{r_{ij}} P_{j1} | \alpha \rangle_1 \dots | \lambda \rangle_i | \mu \rangle_j \dots | \nu \rangle_N = \langle \mu | \langle \lambda | \frac{1}{r_{ij}} | \lambda \rangle_i | \mu \rangle_j \delta_{\alpha\mu} \delta_{\nu\mu} \dots$$

$${}_N \langle \nu | \dots | \mu | \langle \lambda | \dots \langle \alpha | \frac{1}{r_{ij}} P_{ij} | \alpha \rangle_1 \dots | \lambda \rangle_i | \mu \rangle_j \dots | \nu \rangle_N = \langle \mu | \langle \lambda | \frac{1}{r_{ij}} | \lambda \rangle_i | \mu \rangle_j \delta_{\alpha\lambda} \dots \delta_{\nu\mu}$$

↑ Este sí sobrevive

sin λ ni μ

$$\begin{aligned} \langle \phi | H_2 | \phi \rangle &= \sum_{i,j=1}^N \sum_p (-1)^p \langle \phi_H | \frac{1}{r_{ij}} P | \phi_H \rangle \\ &= \sum_{i,j=1}^N \langle \phi_H | \frac{1}{r_{ij}} (1 - P_{ij}) | \phi_H \rangle \\ &= \frac{1}{2} \sum_{\lambda} \sum_{\mu} \langle \lambda \mu | \frac{1}{r_{12}} | \lambda \mu \rangle - \langle \lambda \mu | \frac{1}{r_{12}} | \mu \lambda \rangle \\ &= \frac{1}{2} \sum_{\lambda} \sum_{\mu} J_{\lambda\mu} - K_{\lambda\mu} \end{aligned}$$

$$\langle \phi | H | \phi \rangle = \sum_{\lambda} I_{\lambda} + \frac{1}{2} \sum_{\lambda} \sum_{\mu} [J_{\lambda\mu} - K_{\lambda\mu}]$$

energía
promedio de
 e^- en orbital λ

directo:
repulsión promedio
entre electrones en
orbitales λ y μ

intercambio:
elemento
de matriz
cruzados