

MSE 423 Fall 2025 – Week 6

THE ORIGIN OF BONDING



MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

Last week

- Spherical coordinates and angular momentum
- Commutational relations
- An electron in a central potential:
 - Laplacian in spherical coordinates
 - Separation of variables ($\psi=R\cdot Y$)
 - l -dependent radial equation; effective potential
 - Radial and angular wavefunctions
 - Nodal surfaces
 - Three quantum numbers
 - The alphabet soup: all the possible orbitals for any n, l, m
- Orbital levels, emission and absorption lines
- Stern-Gerlach experiment, spin operators, spin quantum number

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column bar stacked ascending order descending order Values per order Value per grade Comments download Summary download

Year 2025-2026
 Course Fundamentals of solid-state materials
 Questionnaire Indicative feedback of teaching (since 2022-2023)
 Nb Registered 57
 Nb Answered 16

Preliminary feedback

The running of the course enables my learning and an appropriate class climate

Response	Percentage
No opinion	0%
Strongly disagree	0%
Disagree	0%
Agree	44%
Strongly agree	56%

Remarks (5 remarks(s))

- A quick remark, for the class on thursday, we have all our classes of the day in MXF, so I think for all of us it would be better to stay in this classroom on Thursday#8217;s.
- I really appreciate that the teacher takes time to explain the concepts. I would like the correction of the homework to be posted at the beginning of the weekend so that we can make a summary of the week class knowing the answer of the corresponding exercises.
- I think it is not necessary that the TAs take 10 minutes to explain the exercises at the beginning of the exercise session. As we have only 1h to ask our questions, it would more interesting to have more time to ask our questions, because in any case we will read the exercise sheet again. I also think that for most of the people, the class MXFI is more convenient, because we have lecture in this auditorium before and after solid state course.
- Nicola Marzari is without the shadow of a doubt a bulking mad individual. This is one of the reasons why I feel like his course is a time machine to the beginning of the 20th century, where I would be discussing with charismatic geniuses in the veins of Einstein, Planck or Heisenberg (the latter being a bit of a nazi but still) about the grand mysteries of the world. I enjoy the slow pace of the course and Nicola's deep voice, as well as finally understanding (better) where the quantum numbers and orbital theory come from. Cheers.
- The course is great and the jokes are well appreciated. It would be good to return in MX amphi the Thursday because most of the students have course in the same room before and after the course. For the Tuesday the room in MED is good.
- The course is very abstract and mathematical, the concepts hard to understand. Thus, the exercise sessions are also relatively difficult. How the slides are given is nice because we can follow the reasoning of the teacher. Concerning the exam, I am still not sure about how to proceed to review my notes because I don't know what questions to expect.
- The professor explains things slowly and clearly. The content is complex but the class is taught in a relaxed way that allows for questions and interactions with the teaching team.

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Spin Eigenvalues/Eigenfunctions

- Norm (s integer \rightarrow bosons, half-integer \rightarrow fermions)

$$\hat{S}^2 \Psi_{spin} = \hbar^2 s(s+1) \Psi_{spin}$$

- Z-axis projection (electron is a fermion with $s=1/2$)

$$\hat{S}_z \Psi_{spin} = \pm \frac{\hbar}{2} \Psi_{spin}$$

- Spin-orbital: product of the "space" wavefunction and the "spin" wavefunction

Pauli Exclusion Principle

We can't have two electrons in the same quantum state →

Any two electrons in an atom cannot have the same 4 quantum numbers n, l, m, m_s

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Atomic Units

$$m_e=1, e=1, a_0 \text{ (Bohr radius)}=1, \quad \hbar = 1$$

$$\epsilon_0 = \frac{1}{4\pi}$$

$$\text{Energy of 1s electron} = -\frac{1}{2} \frac{Z^2}{n^2}$$

$$(1 \text{ atomic unit of energy} = 1 \text{ Hartree} = 2 \text{ Rydberg} = 27.21 \text{ eV})$$

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Two-electron atom

$$\left[-\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right] \psi(\vec{r}_1, \vec{r}_2) = E_{el} \psi(\vec{r}_1, \vec{r}_2)$$

Many-electron atom

$$\left[-\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_i \sum_{j>i} \frac{1}{|\vec{r}_i - \vec{r}_j|} \right] \psi(\vec{r}_1, \dots, \vec{r}_n) = E_{el} \psi(\vec{r}_1, \dots, \vec{r}_n)$$

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Energy of a collection of atoms

$$\hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{e-e} + \hat{V}_{N-N} + \hat{V}_{e-N}$$

- T_e : quantum kinetic energy of the electrons
- V_{e-e} : electron-electron interactions
- V_{N-N} : electrostatic nucleus-nucleus repulsion
- V_{e-N} : electrostatic electron-nucleus attraction (electrons in the field of all the nuclei)

$$\hat{T}_e = -\frac{1}{2} \sum_i \nabla_i^2 \quad \hat{V}_{e-N} = \sum_i \left[\sum_I V(\vec{R}_I - \vec{r}_i) \right] \quad \hat{V}_{e-e} = \sum_i \sum_{j>i} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

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Hartree Equations

$$\psi(\vec{r}_1, \dots, \vec{r}_n) = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\cdots\phi_n(\vec{r}_n)$$

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Hartree Equations

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Spin-statistics connection

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Spin-statistics connection

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Slater determinant

- An antisymmetric wavefunction is constructed via a Slater determinant of the individual orbitals (instead of just a product, as in the Hartree approach)

$$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_\alpha(\vec{r}_1) & \phi_\beta(\vec{r}_1) & \cdots & \phi_\nu(\vec{r}_1) \\ \phi_\alpha(\vec{r}_2) & \phi_\beta(\vec{r}_2) & \cdots & \phi_\nu(\vec{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_\alpha(\vec{r}_n) & \phi_\beta(\vec{r}_n) & \cdots & \phi_\nu(\vec{r}_n) \end{vmatrix}$$

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Hartree-Fock Equations

The Hartree-Fock equations are, again, **obtained from the variational principle**: we look for the minimum of the many-electron Schrodinger equation in the class of all wavefunctions that are written as a single Slater determinant

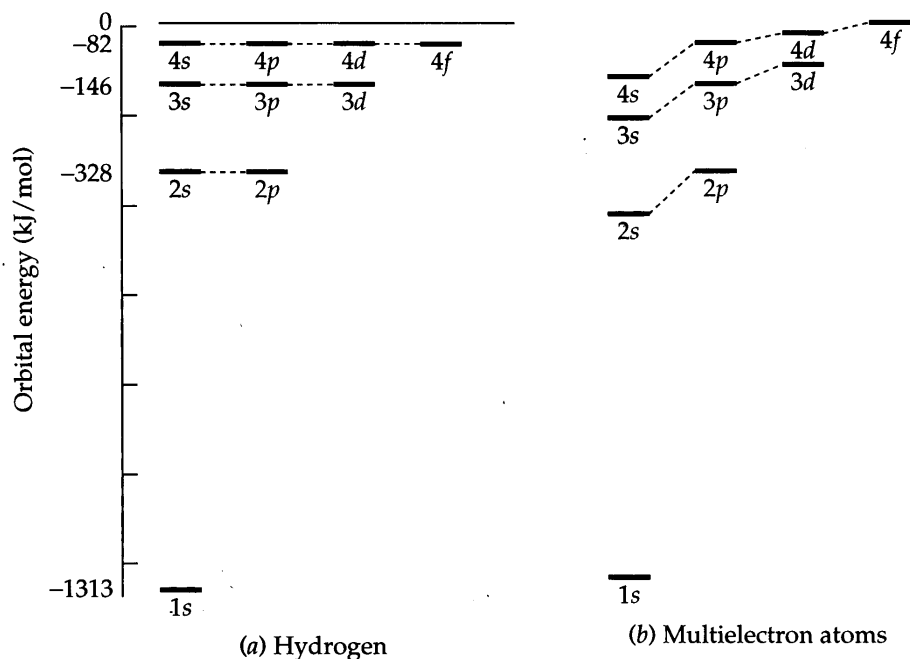
$$\begin{aligned} \psi(\vec{r}_1, \dots, \vec{r}_n) = & \text{Slater} \\ \left[-\frac{1}{2} \nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i) \right] \phi_\lambda(\vec{r}_i) + \\ & \left[\sum_\mu \int \phi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \phi_\mu(\vec{r}_j) d\vec{r}_j \right] \phi_\lambda(\vec{r}_i) - \\ & \sum_\mu \left[\int \phi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \phi_\lambda(\vec{r}_j) d\vec{r}_j \right] \phi_\mu(\vec{r}_i) = \varepsilon \phi_\lambda(\vec{r}_i) \end{aligned}$$

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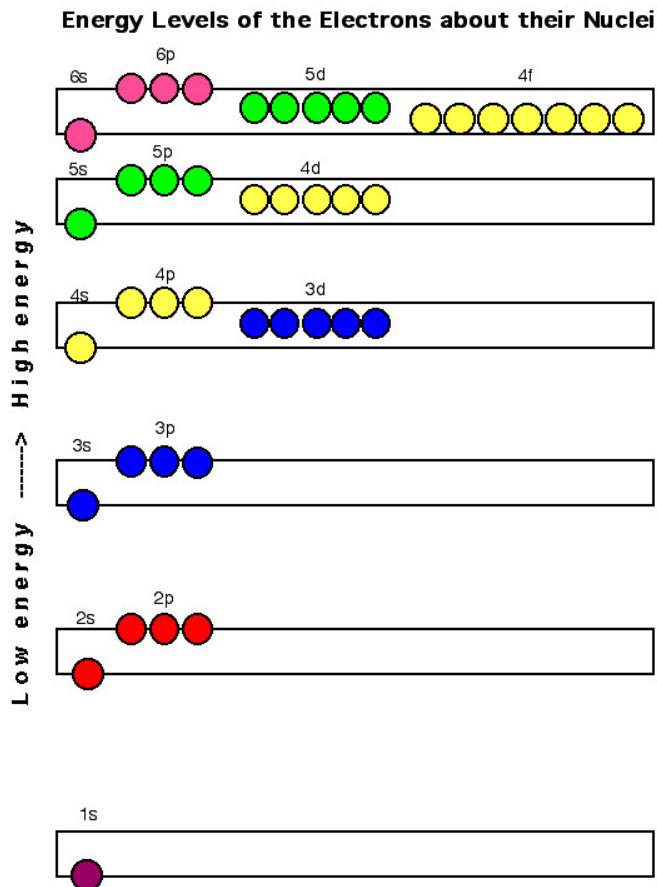
Pauli Exclusion Principle

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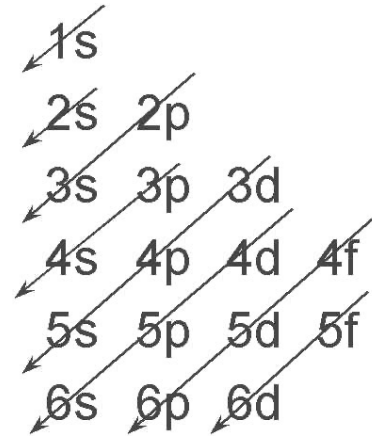
Orbital levels in multi-electron atoms



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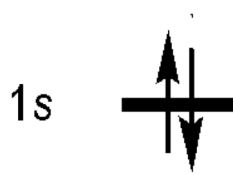


Auf-bau



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One more complexity – spin orbitals

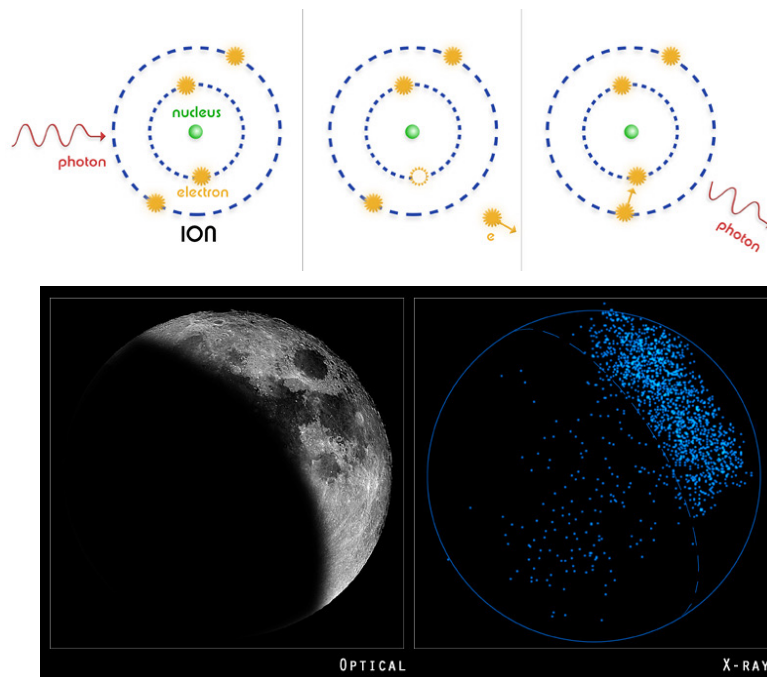


$$|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2) \end{vmatrix}$$

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} \underbrace{[\varphi_{1s}(1)\varphi_{1s}(2)]}_{\text{spatial component}} \underbrace{[\alpha(1)\beta(2) - \alpha(2)\beta(1)]}_{\text{spin component}}$$

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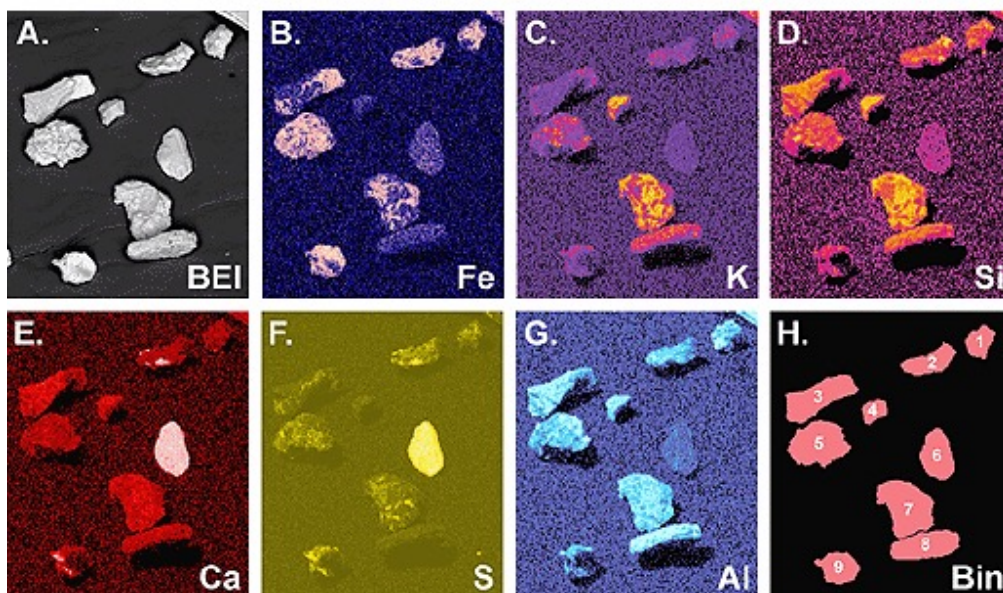
XPS in Materials



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Composition Analysis

X-RAY ELEMENT MAPS OF MINE WASTE SOIL PARTICLES



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Hydrogen Molecular Ion H_2^+

- Born-Oppenheimer approximation: the electron is always in the ground state corresponding to the instantaneous ionic positions

$$\left[-\frac{1}{2} \nabla^2 + \left(\frac{1}{|\vec{R}_{H_1} - \vec{R}_{H_2}|} - \frac{1}{|r - \vec{R}_{H_1}|} - \frac{1}{|r - \vec{R}_{H_2}|} \right) \right] \psi(\vec{r}) = E\psi(\vec{r})$$

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Linear Combination of Atomic Orbitals

- Most common approach to find out the ground-state solution – it allows a meaningful definition of “hybridization”, “bonding” and “anti-bonding” orbitals.
- Also known as LCAO, LCAO-MO (for molecular orbitals), or tight-binding (for solids)
- Trial wavefunction is a linear combination of atomic orbitals – the variational parameters are the coefficients:

$$\Psi_{trial} = c_1 \Psi_{1s}(\vec{r} - \vec{R}_{H_1}) + c_2 \Psi_{1s}(\vec{r} - \vec{R}_{H_2})$$

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How do we find the two coefficients?

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Bonding and Antibonding (I)

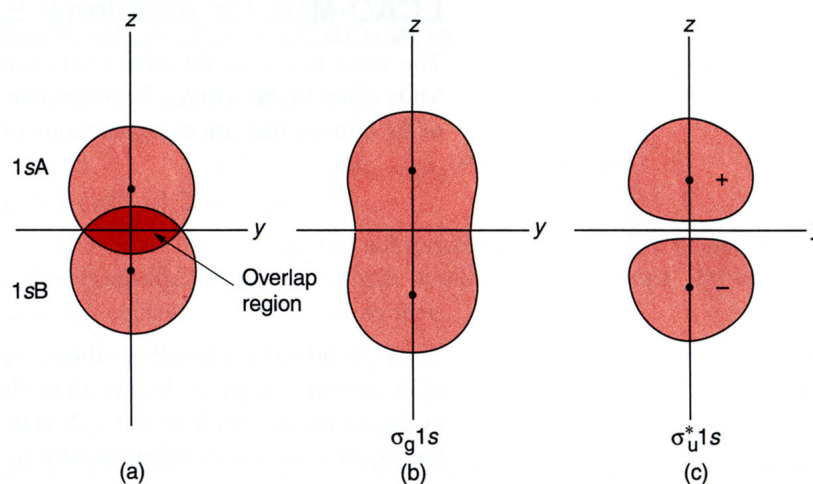


Figure 18.7 The Orbital Region for the $\sigma_g 1s$ and $\sigma_u^* 1s$ LCAO Molecular Orbitals. (a) The overlapping orbital regions of the 1sA and 1sB atomic orbitals. (b) The orbital region of the $\sigma_g 1s$ LCAO-MO. (c) The orbital Region of the $\sigma_u^* 1s$ LCAO-MO. The orbital regions of the LCAO molecular orbitals have the same general features as the "exact" Born Oppenheimer orbitals whose orbital regions were depicted in Figure 18.4.

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Bonding and Antibonding (II)

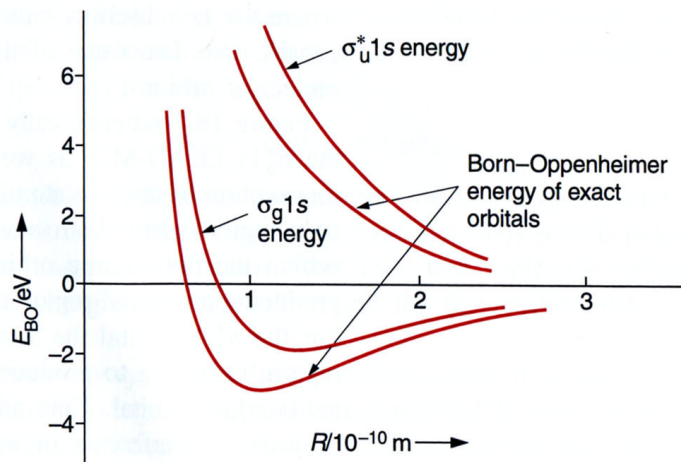


Figure 18.8 The Orbital Energies for the $\sigma_g 1s$ and $\sigma_u^* 1s$ LCAO Molecular Orbitals. This diagram shows qualitatively how the Born–Oppenheimer energies of the LCAO molecular orbitals compare with the Born–Oppenheimer energies of the “exact” orbitals. The approximate orbital energies must lie above the corresponding exact energies for all internuclear distances.

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Formation of a Bonding Orbital

<http://winter.group.shef.ac.uk/orbitron/>



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Formation of a Bonding Orbital



Formation of an Antibonding Orbital

