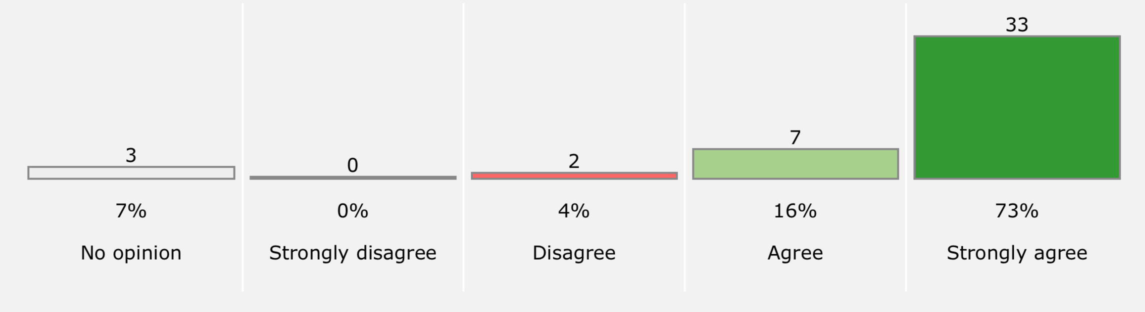
Last week

- An electron in a central potential:
  - Laplacian in spherical coordinates
  - Separation of variables (ψ=RY)
  - 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
- Pauli exclusion principle

Year	2024-2025
Course	Fundamentals of solid-state materials
Questionnaire	Indicative feedback of teaching (since 2022-2023)
Nb Registered	65
Nb Answered	45

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



•Annotations are very unclear, but class is good

•As an SIQ student, this course has not really thought me anything until now. The teacher is really good, and I think when we'll start doing thing that i'm unfamiliar with it will be a very good course. I feel a bit bad about showing up to course and then spending most of the time on my phone, but the teacher gives very good and intuitive insights on things that we learned mathematically in QM1. very good course for someone who's not familiar with qunatum physics

•Hard but very interesting course, I feel like a grown up when writing psis when I do the exercises

•I find the course well structured and clear. The exercises are really helpful to better understand the matter. No negative point to add.

•I really appreciate the way the course is taught. There are few slides but they are intense and go straight to the point. Also the fact that the course is recorded is nice in case we are sick or unable to come to campus at some point.

•I really enjoy lectures for this class. The professor is engaging and also explains the topic very well, so I feel like I understand everything he is talking about. I feel like I am learning a lot in this class and overall I enjoy it very much!

•I think that the course is well taught, the exercises allow to understand better the course content, but I really don't like the subject. I don't understand why this specific topic is part of the mandatory block. It is very fundamental and I don't see how to apply it to materials engineering.

•It would be great if the solution of the exercice could arrive before the weekend so we can correct them during the weekend

•Lectures are clear and well organized. Only complaint is that the professor's handwriting is difficult to read.

•More in class examples and problem solving would be helpful.

•Quite well designed and professor's attention to detail is very commendable. Helped me see connections between theory and consequences, in a much better way than I had seen before.

•Really enjoy the course and the professor’s good attitude.

•The course is incredibly well given ! A very complex topic is turned into a very intuitive subject, thank you!

•The lectures are impressively good. The professor is really breaking down every concept at base level, providing his understanding of it and asking for ours, while including humor from times to times, which makes the learning even pleasant. Hence, I am considering asking for a Project in Material Science II at the THEOS. Also the live broadcasting of the lectures is extremely useful.

•The professor is good at explaining and has impeccable humour that helps keep us concentrated.

•Too difficult course, and not much going on during recitations

•Très bon cours, quelque peu fastidieux mais très bien donné ! Que ce soit le professeur ou les assistants, c'est du très bon travail. Merci

•Very well planned course, the lectures and clear and the concepts very well explained; The exercise sheets are definitely useful in order to fully understand and apply the concepts seen in class (not sure if it's already the case but it would be even better if there were some exercises taken from previous exams)

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

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

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)

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

Hartree Equations

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

Hartree Equations

Spin-statistics connection

Spin-statistics connection

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)

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

Hartree-Fock Equations

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

$$\psi(\vec{r}_1,\ldots,\vec{r}_n)=\left\|Slater\right\|$$

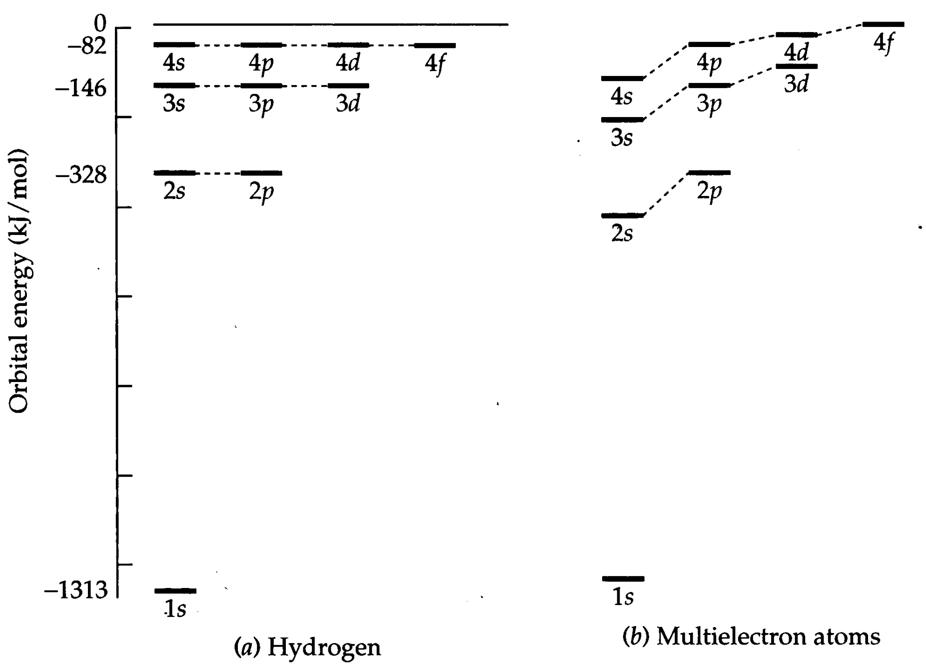
$$\left[-\frac{1}{2}\nabla_i^2+\sum_I V(\vec{R}_I-\vec{r}_i)\right]\varphi_\lambda(\vec{r}_i)+$$

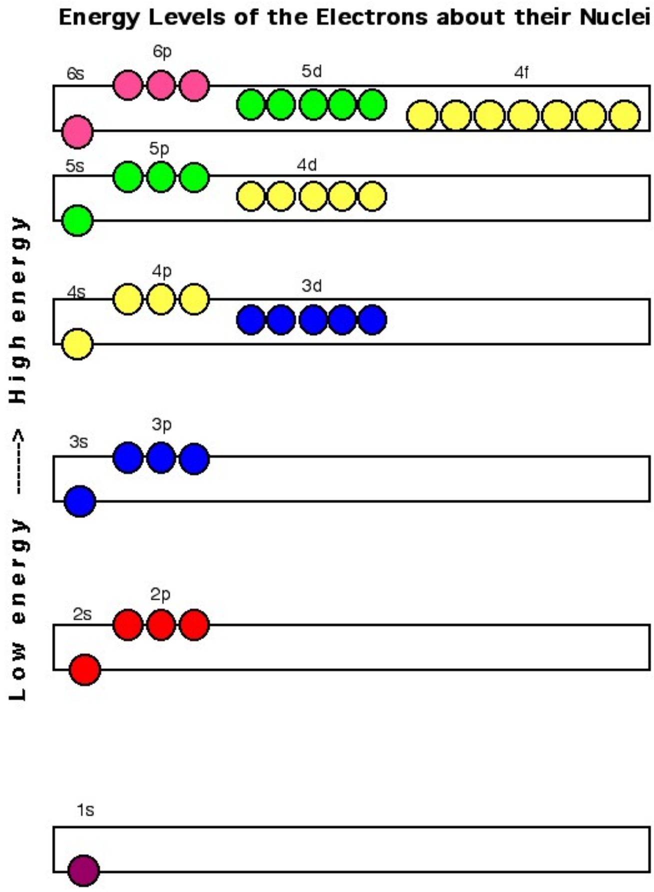
$$\left[\sum_\mu \int \varphi_\mu^*(\vec{r}_j)\frac{1}{|\vec{r}_j-\vec{r}_i|}\varphi_\mu(\vec{r}_j)\,d\vec{r}_j\right]\varphi_\lambda(\vec{r}_i)-$$

$$\sum_\mu\left[\int \varphi_\mu^*(\vec{r}_j)\frac{1}{|\vec{r}_j-\vec{r}_i|}\varphi_\lambda(\vec{r}_j)\,d\vec{r}_j\right]\varphi_\mu(\vec{r}_i)=\varepsilon\varphi_\lambda(\vec{r}_i)$$

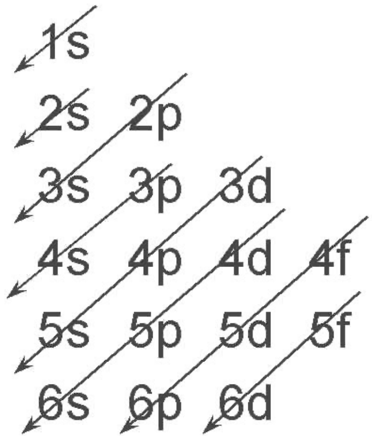
Pauli Exclusion Principle

Orbital levels in multi-electron atoms

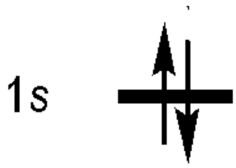




Auf-bau



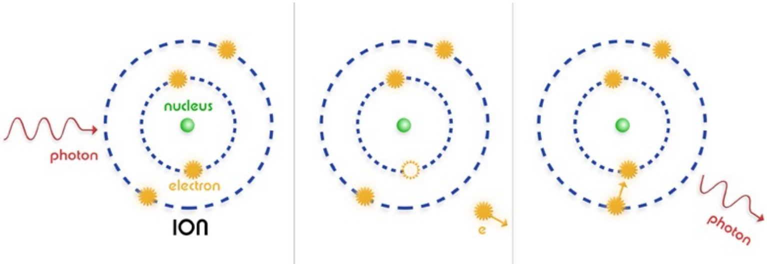
One more complexity – spin orbitals

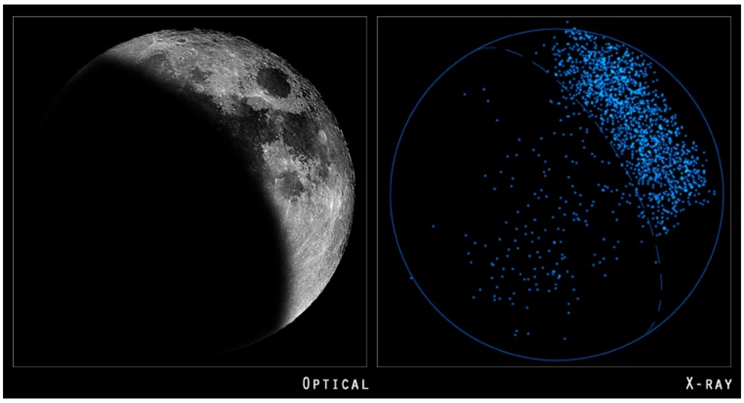


$$|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2) \end{vmatrix}$$

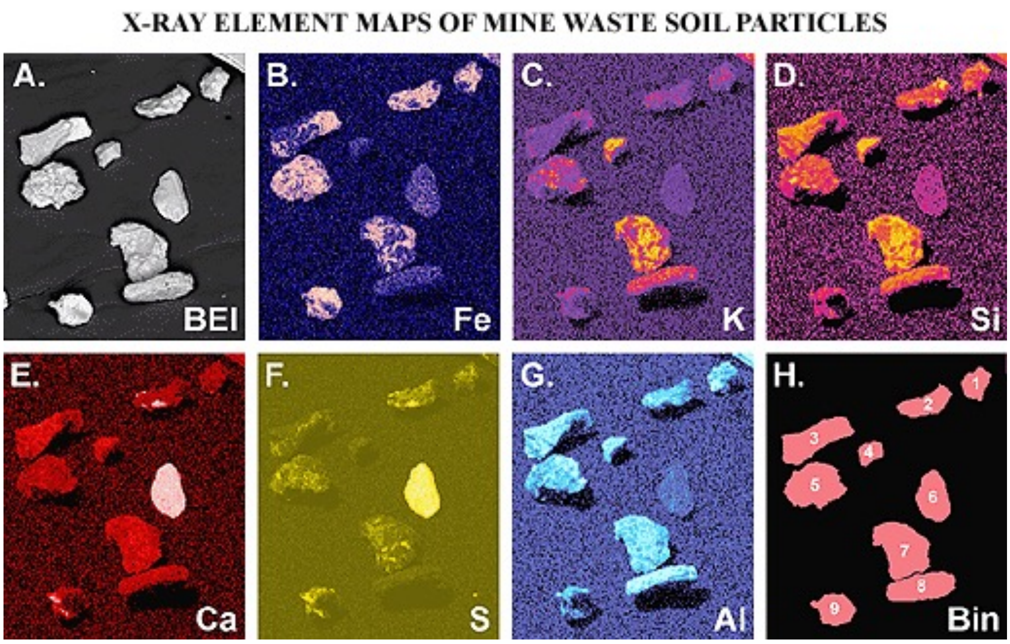
$$|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} \underbrace{[\varphi_{1s}(1)\varphi_{1s}(2)]}_{\text{spatial component}} \underbrace{[\alpha(1)\beta(2) - \alpha(2)\beta(1)]}_{\text{spin component}}$$

XPS in Materials





Composition Analysis



Hydrogen Molecular Ion H_2^+

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

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

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 knows 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:

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

How do we find the two coefficients?

Bonding and Antibonding (I)

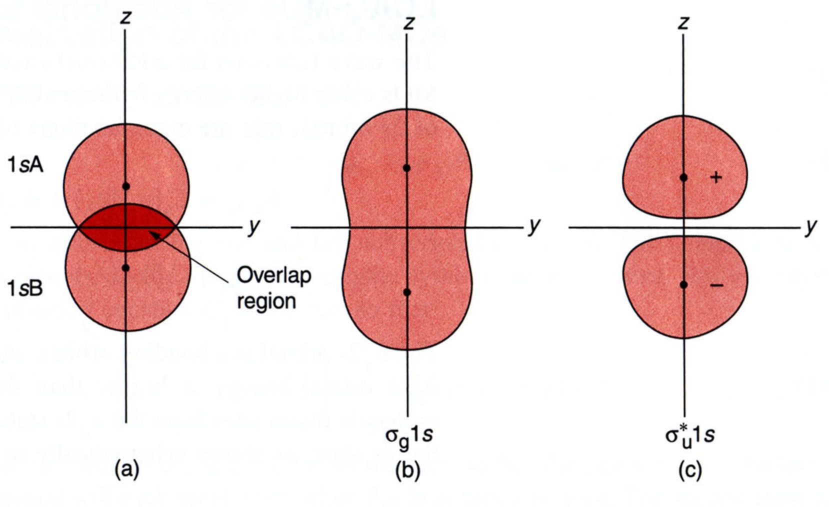


Figure 18.7 The Orbital Region for the $\sigma_g 1s$ and $\sigma_u^* 1s$ LCAO Molecular Orbitals. (a) The overlapping orbital regions of the 1*s*A and 1*s*B atomic orbitals. (b) The orbital region of the $\sigma_g 1s$ LCAO-MO. (c) The orbital Region of the $\sigma_u^* 1s$ LCAO-MO. The orbital regions 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.

Bonding and Antibonding (II)

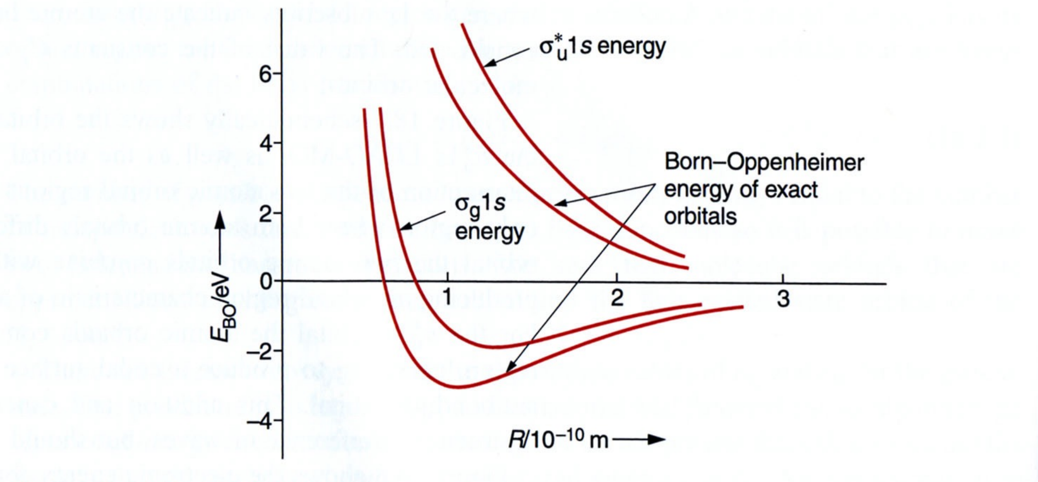


Figure 18.8 The Orbital Energies for the $\sigma_g 1s$ and $\sigma_u^* 1s$ LCAO Molecular Orbitals. This diagram shows qualitatively how the Born–Oppenheimer energies of the LCAO molecular orbitals compare with the Born Oppenheimer energies of the "exact" orbitals. The approximate orbital energies must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

Formation of a Bonding Orbital

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

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2024)

Formation of a Bonding Orbital

Formation of an Antibonding Orbital

Formation of an Antibonding Orbital