CHEM20212

Computational Chemistry II: Fundamentals of electronic structure theory

1 Electronic structure of atoms



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Course Overview

 Electronic structure of atoms Introduction Hydrogenic atoms Multi-electron atoms Ground <i>vs.</i> excited states 	 4 Hückel theory Constructing a Hückel matrix Molecular orbitals Benzene anion Electrophilic and nucleophilic attack
 2 Electronic structure of molecules Molecular orbitals Molecular electronic structure Energy hierarchy 	 5 Spin Hamiltonians A "how-to" guide Matrix elements Example: S = 1/2 Example: S = 1
 3 Matrix mechanics Vector (Hilbert) spaces Bra-ket notation Operators and expectation values Matrix diagonalisation 	6 Workshop

Intended learning objectives

- 1. Construct approximate wave functions for single and multi-electron atoms
- 2. Explain the energy hierarchy of multi-electron atoms
- 3. Differentiate the concepts of ground and excited electronic states, including spin and orbital states
- 4. Mathematically expand and visualise the spatial wave functions of atoms and simple molecules as a linear combination of MOs and basis functions
- 5. Mathematically describe the connection between matrix diagonalisation and solution to the Schrödinger equation
- 6. Construct a Hückel Hamiltonian matrix
- 7. Employ Bra-Ket notation to evaluate the matrix elements of a simple spin Hamiltonian

- What is the goal of computational chemistry?
 - Chemistry is all about electrons
 - We want to know where they spend their time
 - This governs reactivity and physical properties
- Uses fundamental equations of nature and computational techniques to solve chemical problems



- What can you calculate with computational chemistry?
 - Electronic structure
 - Molecular geometry
 - Vibrational modes
 - Excited states
 - Reaction barriers
 - Transition states
 - Molecular dynamics
 - Magnetic properties
 - NMR spectra
 - ...and much more!



- Why is computational chemistry useful?
 - Help explain experimental results
 - "What vibrational mode gives that IR peak?"
 - Quick test before trying experiment
 - "Will this drug bind to this protein?"
 - Do chemistry that is too expensive or dangerous
 - "How does radioactive waste react with steel?"
 - "Which explosive will have a bigger boom?"
 - Do experiments that cannot be performed in reality
 - "Where do the electrons move first in this reaction?"

- How does computational chemistry work?
 - 1. Take molecular structure (guess or from X-Ray structure)
 - 2. Guess molecular orbitals
 - 3. Calculate electronic structure
- ➤ 4. Refine molecular orbitals
 - 5. Refine molecular structure (optional)
 - 6. Calculate electronic structure
 - 7. Is solution consistent?

Repeat

• The central theory? Schrödinger's wave equation:

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

• Hamiltonian operator measures the energy of the wavefunction

- Let's start with a simple problem you know already: hydrogen
 - One nucleus, one electron, spherical symmetry
 - Ignore the nuclear wavefunction: the nucleus is very heavy compared to the electron; basically, it doesn't move!
- Electronic Schrödinger Hamiltonian in spherical coordinates (you've seen this is CHEM10212 last year!):

$$\widehat{H} = -\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

Can manipulate to have individual terms for *r*, θ and φ:
 Ψ is separable!

$$\widehat{H} = -\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

Can manipulate to have individual terms for r, θ and φ:
 Ψ is separable!

$$\Psi = \psi_{n,l,m_l}[r,\theta,\phi] = R_{n,l}[r]Y_{l,m_l}[\theta,\phi]$$

- $-R_{n,l}[r]$ is the radial function for quantum numbers n and l
- $Y_{l,m_l}[\theta, \phi]$ are the spherical harmonics (angular function)
- $-\psi$ is the *spatial single electron wavefunction*

FEED FORWARD: Don't forget $n = 1, 2, ...; l = 0 - n - 1; m_l = -l - l$

- But what about the electron spin?
 - Can have two possible values: $m_s = \pm \frac{1}{2} \left| \frac{\theta_1}{Pu} \right|$
 - *Purely quantum mechanical* (not *actually* spinning) no classical analogue, but can be measured
- Therefore, need to add spin function:

 $\chi_{n,l,m_l,m_s} [r,\theta,\phi,s_z] = \psi_{n,l,m_l} [r,\theta,\phi] \sigma_{m_s} [s_z]$

- The electron spin coordinate is s_z , which is the *projection* of the electron spin on the z-axis, and can only take the values $s_z = \pm \frac{1}{2}$ (in units of \hbar)
- The spin function σ_{m_s}[s_z] = δ_{m_s,s_z} where δ_{m_s,s_z} is the *Kronecker delta*: δ_{m_s,s_z} = 1 if m_s = s_z and 0 if m_s ≠ s_z
 χ is the single electron *spinorbital*

FEED FORWARD: m_s is QN of the spinorbital s_z is spin coordinate of electron *Purely book-keeping*

Electron spin

- The experiment that shows the quantised spin magnetic moment of the electron:
 - 1. Vaporise silver in an oven, shoot atoms towards a screen
 - 2. Apply magnetic field in path of atoms
 - 3. Magnetic particles will be deflected
 - 4. Silver has one unpaired electron: [Kr]4d¹⁰5s¹



Electron spin



All the animations and explanations on www.toutestquantique.fr

http://www.toutestquantique.fr

- Solving the radial equation is non-trivial and is not covered here (but *there is an exact solution for single electron atoms*)
- The energy of the different wavefunction solutions leads to the Rydberg formula $E_n \approx -\frac{RZ^2}{n^2}$ where $R \approx 13.6$ eV (note there is no dependence on l; *i.e.* $E_{2s} = E_{2p} = E_2$)

$$E_{3} \approx -1.5 \text{ eV}$$

$$E_{2} \approx -3.4 \text{ eV}$$
What do negative energies mean?
What is the electron configuration of
hydrogen?
How many states are there for $n = 1$?
How many states are there for $n = 2$?

E

- Helium: one nucleus, two electrons surely it's not that hard?
- Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_{i=1}^2 \left[\frac{1}{r_i^2} \frac{\partial}{\partial r_i} \left(r_i^2 \frac{\partial}{\partial r_i} \right) + \frac{1}{r_i^2 \sin \theta_i} \frac{\partial}{\partial \theta_i} \left(\sin \theta_i \frac{\partial}{\partial \theta_i} \right) + \frac{1}{r_i^2 \sin^2 \theta_i} \frac{\partial^2}{\partial \phi_i^2} \right] \\ - \frac{Ze^2}{4\pi\varepsilon_0} \sum_{i=1}^2 \left[\frac{1}{r_i} \right] + \frac{e^2}{4\pi\varepsilon_0 |\vec{r_1} - \vec{r_2}|}$$

- This term *cannot be separated* into an r_1 part and an r_2 part No exact solution!
 - Must use approximations!

• Assume each electron only interacts with the average position of the other: atom is spherically symmetric, so the other electron looks like a spherical cloud of negative charge



• Hamiltonian (nucleus 'screened' by other electrons, *C*):

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_{i=1}^2 \left[\frac{1}{r_i^2} \frac{\partial}{\partial r_i} \left(r_i^2 \frac{\partial}{\partial r_i} \right) + \frac{1}{r_i^2 \sin \theta_i} \frac{\partial}{\partial \theta_i} \left(\sin \theta_i \frac{\partial}{\partial \theta_i} \right) + \frac{1}{r_i^2 \sin^2 \theta_i} \frac{\partial^2}{\partial \phi_i^2} \right] \\ + \left(-\frac{Ze^2}{4\pi\varepsilon_0} + C \right) \sum_{i=1}^2 \left[\frac{1}{r_i} \right]$$

• This is called *mean field theory*, and can be generalised for molecular calculations (see Hartree-Fock theory)

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_{i=1}^2 \left[\frac{1}{r_i^2} \frac{\partial}{\partial r_i} \left(r_i^2 \frac{\partial}{\partial r_i} \right) + \frac{1}{r_i^2 \sin \theta_i} \frac{\partial}{\partial \theta_i} \left(\sin \theta_i \frac{\partial}{\partial \theta_i} \right) + \frac{1}{r_i^2 \sin^2 \theta_i} \frac{\partial^2}{\partial \phi_i^2} \right] \\ + \left(-\frac{Ze^2}{4\pi\varepsilon_0} + C \right) \sum_{i=1}^2 \left[\frac{1}{r_i} \right]$$

- Without the troublesome term, the equation is now separable
 - solutions are known as the *Hartree product*:

$$\Psi[\overrightarrow{x_1}, \overrightarrow{x_2}] = \chi_{\kappa_1}[\overrightarrow{x_1}]\chi_{\alpha_2}[\overrightarrow{x_2}]$$
$$-\overrightarrow{x_i} \equiv (r_i, \theta_i, \phi_i, s_{z_i}) \text{ and } \kappa_i \equiv (n_i, l_i, m_{l_i}, m_{s_i})$$

• However, this does not obey the Pauli antisymmetry (exclusion) principle: *"The wavefunction must be anti-symmetric under the exchange of electrons"*. Mathematically:

 $\Psi[\overrightarrow{x_1}, \overrightarrow{x_2}] = -\Psi[\overrightarrow{x_2}, \overrightarrow{x_1}]$ Let's see this fail by hand...

• To satisfy Pauli, we need a combination of Hartree products where coordinates are switched:

$$\Psi[\overrightarrow{x_1}, \overrightarrow{x_2}] = \frac{1}{\sqrt{2}} \left(\chi_{\kappa_1}[\overrightarrow{x_1}] \chi_{\kappa_2}[\overrightarrow{x_2}] - \chi_{\kappa_1}[\overrightarrow{x_2}] \chi_{\kappa_2}[\overrightarrow{x_1}] \right)$$

• General solution known as a *Slater determinant*:

$$\Psi[\overrightarrow{x_{1}}, \overrightarrow{x_{2}}, \dots, \overrightarrow{x_{N}}] = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_{\kappa_{1}}[\overrightarrow{x_{1}}] & \chi_{\kappa_{2}}[\overrightarrow{x_{1}}] & \cdots & \chi_{\kappa_{N}}[\overrightarrow{x_{1}}] \\ \chi_{\kappa_{1}}[\overrightarrow{x_{2}}] & \chi_{\kappa_{2}}[\overrightarrow{x_{2}}] & \cdots & \chi_{\kappa_{N}}[\overrightarrow{x_{2}}] \\ \vdots & \vdots & \ddots & \vdots \\ \chi_{\kappa_{1}}[\overrightarrow{x_{N}}] & \chi_{\kappa_{2}}[\overrightarrow{x_{N}}] & \cdots & \chi_{\kappa_{N}}[\overrightarrow{x_{N}}] \end{vmatrix}$$

- Columns have same spinorbital, rows have same coordinates

Ν

- If two columns are identical, the determinant is zero.
- Thus, antisymmetry enforces the Pauli exclusion principle!

- With more than one electron, orbital energies depend on *l*This is why 1s fills first, followed by 2s, followed by 2p, *etc*.
- Atoms also have high electronic degeneracy



• What is the ground state degeneracy?



15 states!

- But are all 15 states *actually* the same energy?
 - No! Electrons repel each other! $\left(\frac{1}{|\vec{r}_1 \vec{r}_2|}\right)$
 - Configurations are spit into *terms* (CHEM10101)
 - Terms are classified by $S = \sum_{i} m_{s_i}$ and $L = \sum_{i} m_{l_i}$ and written as ${}^{2S+1}L$ (*L* in spectroscopic notation, S, P, D, *etc.*)

 $S = \frac{1}{2} + \frac{1}{2} = 1, L = 1 + 0 = 1$ $m_l = +1$ $m_l = 0$ $m_l = -1$ Must have ³P term! Degeneracy = 3×3

2*L* + 1

$$m_l = +1 \quad m_l = 0 \quad m_l = -1$$

$$S = \frac{1}{2} - \frac{1}{2} = 0, L = 1 + 1 = 2$$

Must have ¹D term! Degeneracy = 1×5 = 5

One state missing: must have ${}^{1}S$ term! Degeneracy = $1 \times 1 = 1$

