CHEM20212
Computational Chemistry II:
Fundamentals of electronic structure theory

1 Electronic structure of atoms

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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
Introduction to computational chemistry

• 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

Molecular structure  →  Electronic structure
Introduction to computational chemistry

• 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!
Introduction to computational chemistry

- 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?

The central theory? Schrödinger’s wave equation:

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

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 in CHEM10212 last year!):

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

Can manipulate to have individual terms for \( r \), \( \theta \) and \( \phi \):
\( \Psi \text{ is separable!} \)
Hydrogenic atoms

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

- Can manipulate to have individual terms for \( r, \theta \) and \( \phi \): \( \Psi \) 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 \( n = 1,2,\ldots; l = 0 - n-1; m_l = -l – l \)
Hydrogenic atoms

• But what about the electron spin?
  – Can have two possible values: \( m_s = \pm \frac{1}{2} \)
  – *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 \( \sigma_{m_s}[s_z] = \delta_{m_s,s_z} \) where \( \delta_{m_s,s_z} \) is the
    *Kronecker delta*: \( \delta_{m_s,s_z} = 1 \) if \( m_s = s_z \) and 0 if \( m_s \neq s_z \)
  – \( \chi \) is the single electron *spinorbital*
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]4d^{10}s^{1}

Classical spin: *continuous distribution*

Quantum spin: *discrete distribution*
THE SPIN,
A QUANTUM MAGNET

All the animations and explanations on
www.toutestquantique.fr

http://www.toutestquantique.fr
Hydrogenic atoms

- 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. $E_{2s} = E_{2p} = E_2$).

- $E_3 \approx -1.5$ eV
- $E_2 \approx -3.4$ eV
- $E_1 \approx -13.6$ 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 $n = 2$?**
Multi-electron atoms

• 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!
Multi-electron atoms

- 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)
Multi-electron atoms

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

\[ + \left( -\frac{Ze^2}{4\pi\varepsilon_0} + C \right) \sum_{i=1}^{2} \left[ \frac{1}{r_i} \right] \]

- Without the troublesome term, the equation is now separable – solutions are known as the **Hartree product**: 
  
  \[ \Psi[\vec{x}_1, \vec{x}_2] = \chi_{\kappa_1} [\vec{x}_1] \chi_{\alpha_2} [\vec{x}_2] \]

  - \( \vec{x}_i \equiv (r_i, \theta_i, \phi_i, s_{zi}) \) 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:

  \[ \Psi[\vec{x}_1, \vec{x}_2] = -\Psi[\vec{x}_2, \vec{x}_1] \quad \text{Let's see this fail by hand…} \]
Multi-electron atoms

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

\[ \Psi[\vec{x}_1, \vec{x}_2] = \frac{1}{\sqrt{2}} \left( \chi_{\kappa_1}[\vec{x}_1] \chi_{\kappa_2}[\vec{x}_2] - \chi_{\kappa_1}[\vec{x}_2] \chi_{\kappa_2}[\vec{x}_1] \right) \]

• General solution known as a *Slater determinant*:

\[ \Psi[\vec{x}_1, \vec{x}_2, ..., \vec{x}_N] = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_{\kappa_1}[\vec{x}_1] & \chi_{\kappa_2}[\vec{x}_1] & \cdots & \chi_{\kappa_N}[\vec{x}_1] \\ \chi_{\kappa_1}[\vec{x}_2] & \chi_{\kappa_2}[\vec{x}_2] & \cdots & \chi_{\kappa_N}[\vec{x}_2] \\ \vdots & \vdots & \ddots & \vdots \\ \chi_{\kappa_1}[\vec{x}_N] & \chi_{\kappa_2}[\vec{x}_N] & \cdots & \chi_{\kappa_N}[\vec{x}_N] \end{vmatrix} \]

- Columns have same spinorbital, rows have same coordinates
- If two columns are identical, the determinant is zero.
- Thus, antisymmetry enforces the Pauli exclusion principle!
Multi-electron atoms

• 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
  – *e.g.* carbon atom $1s^22s^22p^2$:

Which orbital do we draw as empty?

This option is called orbital degeneracy

What is the ground state degeneracy?

FEED FORWARD:

$E_{2s} = E_{2p}$ for H

$E_{2s} < E_{2p}$ for He!
Multi-electron atoms

- What is the ground state degeneracy?

15 states!
Multi-electron atoms

- 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 split 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.)

\[
\begin{align*}
S &= \frac{1}{2} + \frac{1}{2} = 1, \quad L = 1 + 0 = 1 \\
\text{Must have } ^3P \text{ term! Degeneracy } &= 3 \times 3 = 9 \\
S &= \frac{1}{2} - \frac{1}{2} = 0, \quad L = 1 + 1 = 2 \\
\text{Must have } ^1D \text{ term! Degeneracy } &= 1 \times 5 = 5 \\
\text{One state missing: must have } ^1S \text{ term! Degeneracy } &= 1 \times 1 = 1
\end{align*}
\]
Multi-electron atoms

- First two configurations of carbon:
- Ground state term given by Hund’s rules (CHEM10101, CHEM10312)
- Note that orbital energy diagrams are only one part of the story
- Usually only think about ground state, but *don’t forget the excited states exist!*