Quantum Chemistry: The Hidden Rules of Atoms and Molecules

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Roadmap

- Wave function

- Schrödinger Equation

- The Hamiltonian

- Hydrogen Atom

- Helium Atom

    - Independent Particle

    - Perturbation theory

    - Variational method

- Chemical bond: LCAO-MO

- Intermolecular Forces

- Fragmentation approaches

Why Quantum Mechanics?

Quantum mechanics (QM) described the behavior of matter at the smallest scales: molecules, atoms, electrons, photons, quarks,.... Essential to the operation of modern technology. Beautiful subject that took most of the first half of the 20th century to formulate
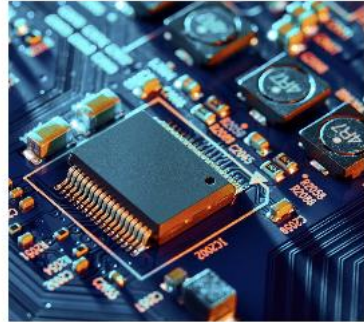
I think I can safely say that nobody understands quantum mechanics. So do not take the lecture too seriously… but just relax and enjoy it… Do not keep saying to yourself, if you can possibly avoid it, "But how can it be like that?" because you will get… into a blind alley from which nobody has escaped. Nobody knows how it can be like that.

The Messenger Lectures, 1964

Feynman

1900 <u>Planck</u> "solves" the blackbody problem by postulating that the oscillators that emit light have quantized energy levels.

"Until after some weeks of the most strenuous work of my life, light came into the darkness, and a new undreamed-of perspective opened up before me...the whole procedure was an act of despair because a theoretical interpretation had to be found at any price, no matter how high that might be."

1905 <u>Einstein</u> proposes that light energy is quantized with quanta called "photons" - waves behave like particles

Photoelectric effect for which he got the Nobel Prize

1913 <u>Bohr</u> proposes that electron orbits are quantized

Idea that electrons act like waves - "explained" H atom, but wrong in crucial ways

1923 <u>de Broglie</u> proposes that particles behave like waves

The step that paved the way for understanding all of nature

1925-1926 <u>Schrödinger</u> postulate the Schrödinger equation
...

Wave Function: State Function of the Quantum Mechanical System

$$\Psi(\boldsymbol{r}, t)$$

- Wave function (Ψ) defines the state of a physical system.

- It doesn't tell you exactly where to find the particle, but where it is likely.

- $|\Psi^2| \rightarrow$ the probability density, the chance of finding an electron at a specific location at t.

- Ψ must be single valued, finite, smoothly varying and continuous

How do we obtain wave functions?

Schrödinger Equation: The Quantum Rulebook

The fundamental equation of quantum mechanics, developed (1926) by Austrian physicist, Erwin Schrödinger

Time-dependent

$$i\hbar \frac{\partial}{\partial t} \Psi(\boldsymbol{r}, t) = \hat{H}\Psi(\boldsymbol{r}, t)$$

Time-independent

$$\hat{H}\Psi(\boldsymbol{r}) = E\Psi(\boldsymbol{r})$$

➔ Stationary-state $\Psi(\boldsymbol{r})$
➔ E: energy of the state (eigenvalue)

Central importance in chemistry

- Postulate: for every observable in classical mechanics (e.g., position, momentum, energy), there corresponds a mathematical operator in quantum mechanics.
- Hamiltonian Operator ($\hat{H}$): quantum mechanical operator for energy

$$\hat{H} = \boxed{-\frac{\hbar^2}{2m}\nabla^2} + \boxed{V(\boldsymbol{r})}$$

K. E.   P. E.

The Hamiltonian

- The Hamiltonian in the time-independent Schrödinger equation has the following form:

$$\widehat{H} = \sum_{i=1}^{N} \widehat{T}_i + \sum_{A=1}^{M} \sum_{i}^{N} \widehat{V}_{iA} + \sum_{i=1}^{N} \sum_{j>i}^{N} \widehat{V}_{ij} + \sum_{A=1}^{M} \widehat{T}_A + \sum_{A=1}^{M} \sum_{B>A}^{M} \widehat{V}_{AB}$$
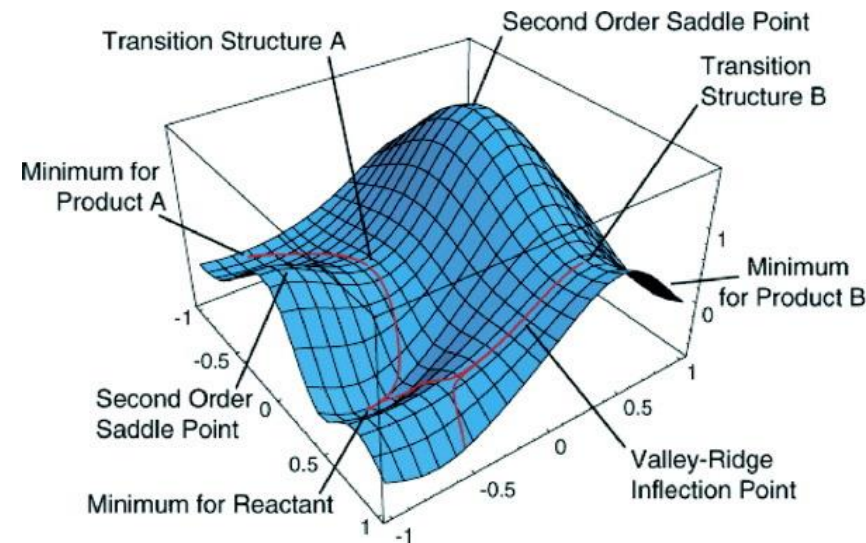
Kinetic energy operator of electron i.

Potential energy operator between nucleus A and electron i. **attractive**

Potential energy operator between electrons i and j. **repulsive**

Born-Oppenheimer approximation: assume nuclei are massive compared to electrons

Schrödinger Equation for Chemistry Problems

- Schrödinger equation is an eigenvalue equation

  - (Operator) eigenfunction = (eigenvalue) eigenfunction

- Our objective is to solve the Schröndinger equation for chemistry problems (atoms, molecules ..)

- Analytic solution only for H atom (1 electron system or hydrogen-like system)

- Not possible for anything with > 1 electrons ➔ Solution: introduce approximations

- Orbitals: one-electron wave function

$$\hat{H}\Psi(\boldsymbol{r}) = E\Psi(\boldsymbol{r})$$

The Roadblock

$$\hat{H} = \sum_{i=1}^{N} \hat{T}_i + \sum_{A=1}^{M} \sum_{i}^{N} \hat{V}_{iA} + \sum_{i=1}^{N} \sum_{j>i}^{N} \hat{V}_{ij}$$

The Schrödinger equation cannot be solved exactly because of the $V_{ij} = {}^{-1}/r_{ij}$

r_{ij} = the distance between electrons i and j = $\left[(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2 \right]^{1/2}$

Not separable → the many-body problem

Hydrogen Atom: can be solved exactly

$$\hat{H} = \hat{T}_1 + \hat{V}_{1A}$$

Only one electron → No V_{ij} term

The wave function solution to the Schrödinger equation for the hydrogen atom defining the orbitals is given by (in <u>spherical polar coordinates</u>):

Eigenfunction: $\qquad \Psi_{n,l,m}(r,\theta,\phi) = R_{n,l}(r) Y_l^m(\theta,\phi)$

Radial function $\qquad\qquad$ Spherical harmonics

n=1,2,3... Principal quantum number
l=0,1,2...n-1 Angular quantum number
|m|≤l Magnetic quantum number
R determines the size/extent of the wave function
Y determines the shape: s, p, d, ...
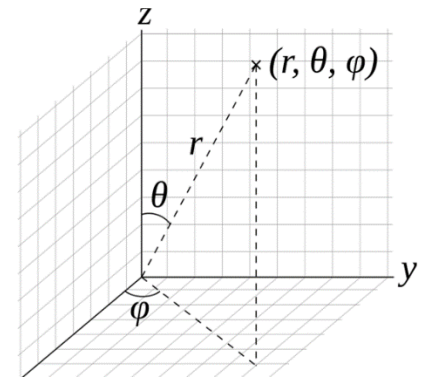
Radial Function and Spherical Harmonics

$$R_{10} = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Zr/a_0}$$

$$R_{21} = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

$$R_{20} = 2\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\left(1 - \frac{Zr}{2a_0}\right) e^{-Zr/2a_0}$$

$$R_{32} = \frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$$

$$R_{31} = \frac{4\sqrt{2}}{3}\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right)\left(1 - \frac{Zr}{6a_0}\right) e^{-Zr/3a_0}$$

$$R_{30} = 2\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(1 - \frac{2Zr}{3a_0} + \frac{2(Zr)^2}{27a_0^2}\right) e^{-Zr/3a_0}$$

Note: $a_0 = 1$ in atomic units

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$$

$$Y_{1,\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi}$$

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_{2,\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{\pm 2i\phi}$$

$$Y_{2,\pm1} = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{\pm i\phi}$$

$$Y_{2,0} = \sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta - 1\right)$$

$$Y_{3,\pm3} = \mp\sqrt{\frac{35}{64\pi}}\sin^3\theta\, e^{\pm 3i\phi}$$

$$Y_{3,\pm2} = \sqrt{\frac{105}{32\pi}}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$$

$$Y_{3,\pm1} = \mp\sqrt{\frac{21}{64\pi}}\sin\theta\left(5\cos^2\theta - 1\right)e^{\pm i\phi}$$

$$Y_{3,0} = \sqrt{\frac{7}{16\pi}}\left(5\cos^3\theta - 3\cos\theta\right)$$

Atomic Orbitals: One-Electron Wave Functions

- One-electron wave function solution to the Schrödinger equation for a single electron
- energy, shape, and orientation of an electron's "probability cloud"
- Spherical harmonics are complex. In order to work with real functions, we take linear combinations of the complex spherical harmonics.

s orbital

p orbitals

d orbitals
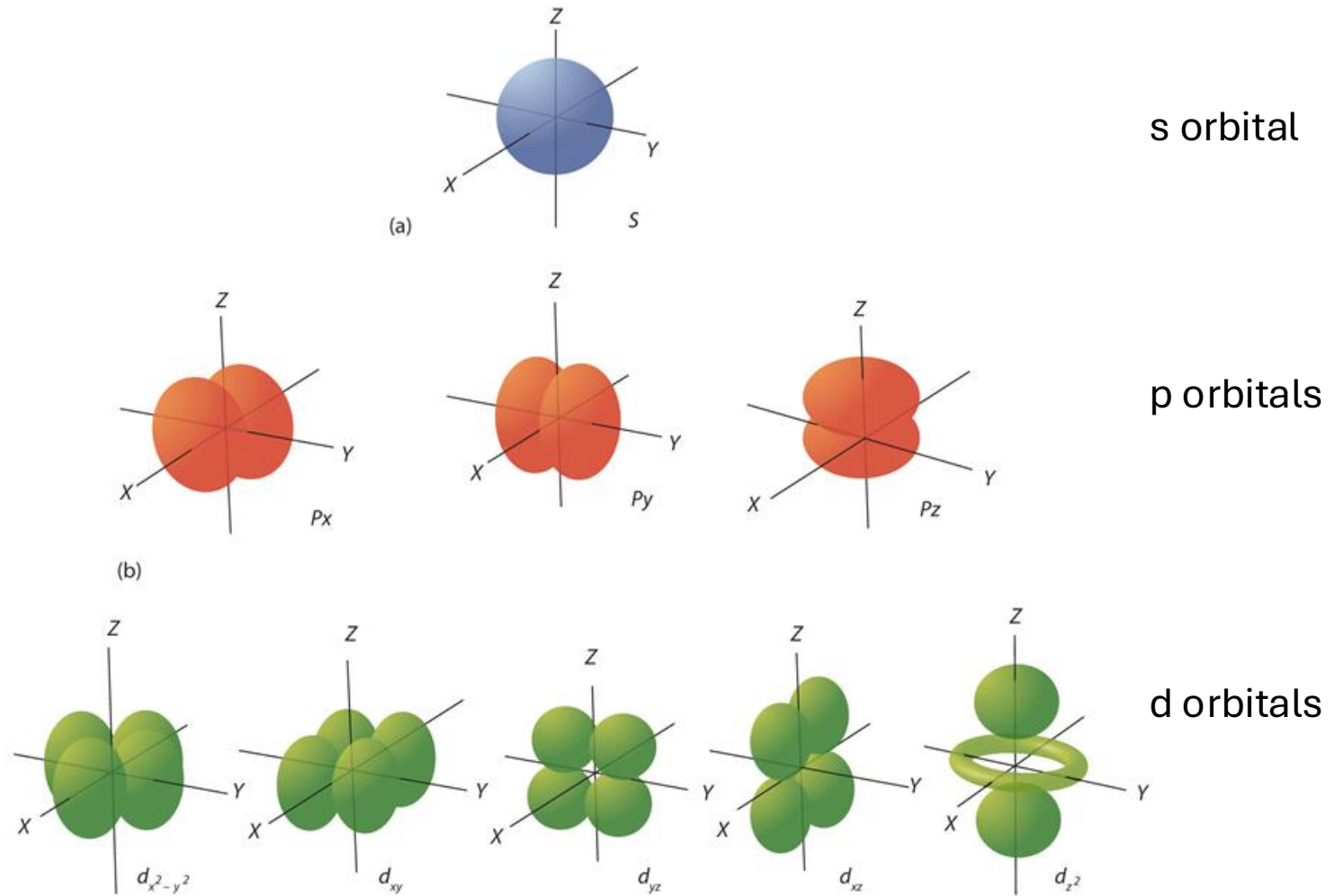
$$\Psi_{n,l,m}(r,\theta,\phi) = R_{n,l}(r)Y_l^m(\theta,\phi)$$

Hydrogen Atom Energy Levels

In SI units, The energy levels of the hydrogen atom are given by:

$$E_n = \frac{-Z^2 \mu e^4}{8\varepsilon_0 n^2 h^2}$$

Z= Number of protons in the nucleus
μ= reduced mass (kg): $m_e m_p / (m_e + m_p)$
e= charge of the proton (C)
n= principal quantum number
h= Plank's constant (J.s)
ε_0=permittivity ($C^2.N^{-1}.m^{-2}$)

In atomic units, the energy levels of the hydrogen atom are given by:

$$E_n = \frac{-Z^2}{2n^2}$$

Note: The energy depends on n only. Not on l and m. Therefore, states with the same n and different l and m (i.e., 2s and 2p) are degenerate. This degeneracy is partly lifted for many-electron atoms

H Atom: Ground State Energy

For ground state, n = 1

$$E_1 = -\frac{Z^2}{2 \times 1^2} = -\frac{1}{2}\,hartree$$

Units: 1 hartree = 27.21 eV = 627.5 kcal/mol

E_n = -1/2 h = -13.6 eV = -313.76 kcal/mol

So, first ionization potential (IP) for H = 13.6 eV

How do we deal with heavier atoms?

Helium Atom: Independent Particle

N = 2 (electrons)

$$\widehat{H} = \sum_{i=1}^{N} \widehat{T}_i + \sum_{A=1}^{M} \sum_{i}^{N} \widehat{V}_{iA} + \sum_{i=1}^{N} \sum_{j>i}^{N} \widehat{V}_{ij} = T_1 + T_2 + V_{1A} + V_{2A} + \boxed{V_{12}}$$

Cannot solve SE exactly due to the electron repulsion term in the Hamiltonian → many-body problem

Independent particle model: Can we ignore the electron repulsion?

$$\widehat{H} = (T_1 + V_{1A}) + (T_2 + V_{2A}) = H_1^{(0)} + H_2^{(0)} = H^{(0)}$$

This Hamiltonian is the sum of two hydrogen-like Hamiltonians that we can solve exactly and separately:

$$\widehat{H}(1)\psi(1) = E_1\psi(1)$$

$$\widehat{H}(2)\psi(2) = E_2\psi(2)$$

$$\Psi = \psi(1)\psi(2)$$

$$E = E_1 + E_2 = -2 \times \frac{Z^2}{2n^2} = -4 \; hartree$$

Z=2 for helium

Experimental: -2.905 Hartree
→ ~ 1.1 Hartree error = 687 kcal/mol
Energy is too low due to neglecting electron repulsion

Helium Atom: Perturbation Theory

Perturbation Theory

Independent particle wave functions (orbitals) as starting point

$1/r_{12}$ as a perturbation to correct the zeroth order Hamiltonian ($H^{(0)}$)

$$\widehat{H} = T_1 + T_2 + V_{1A} + V_{2A} + V_{12}$$

$$\underbrace{\phantom{T_1 + T_2 + V_{1A} + V_{2A}}}_{H^{(0)}} \quad \underbrace{\phantom{V_{12}}}_{H': \text{ perturbation}}$$

$H^{(0)}$ H': perturbation

Using perturbation theory, the first-order correction to the energy is:

$$E^{(1)} = \left\langle \Psi^{(0)} \middle| \widehat{V}_{12} \middle| \Psi^{(0)} \right\rangle = \int \Psi^{(0)*} \widehat{V}_{12} \Psi^{(0)} d\tau = \frac{5}{8} Z = 1.25 \; hartree$$

$$E = E^{(0)} + E^{(1)} = \mathbf{-2.75} \; hartree \qquad \rightarrow \text{Better than the independent particle model}$$

Experimental: -2.905 Hartree

Helium Atom: Variational Method

Variational Principle: The expectation value of the energy for any normalized trial wave function (Φ) is an upper bound to the true ground state energy. The closer Φ is to the exact wave function, the closer $\langle E_{trial} \rangle$ will be to E_0.

$$\langle E_{trial} \rangle = \langle \Phi | \hat{H} | \Phi \rangle \geq E_0$$

Need a trial wave function for He. Where do we get one?
So far, all we know is the orbitals from the independent particle model, may as well try it.

$$\Phi = \psi_{1s}(1)\psi_{1s}(2)$$

$$\psi_{1s}(1) = \frac{1}{\sqrt{\pi}} \zeta^{3/2} e^{-\zeta r_1}$$

$$\psi_{1s}(2) = \frac{1}{\sqrt{\pi}} \zeta^{3/2} e^{-\zeta r_2}$$

Effective atomic number:
Variational parameter

If ζ=Z=2 → get the same result as using perturbation theory

Want to find the value of ζ to give the lowest energy

$$\rightarrow \zeta = \frac{27}{16} \cong 1.69 < 2$$

Each electron partially screens the nucleus from the other so that the net effective nuclear charge is reduced from 2 to 27/16

$$\rightarrow \langle E_{trial} \rangle = -\mathbf{2.85} \text{ hartree}$$

Experimental: -2.905 Hartree

Chemical Bond: Quantum Glue
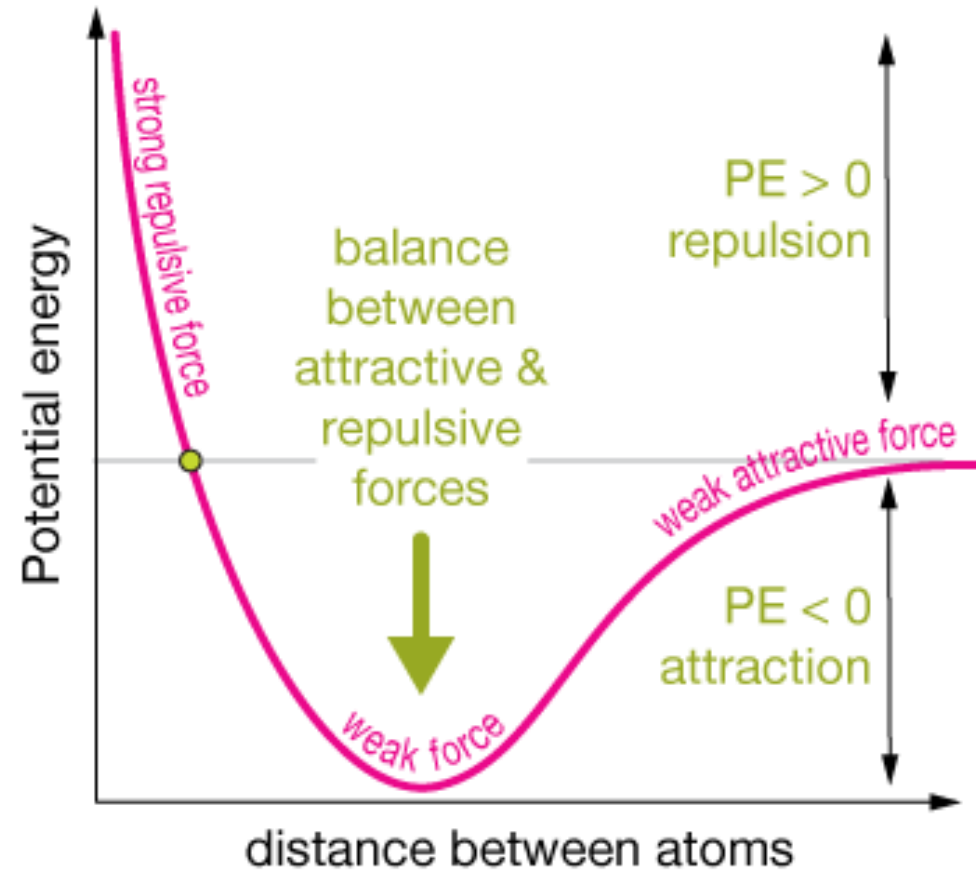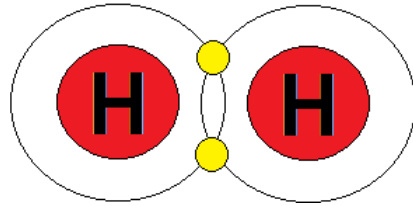
# Linear Combination of Atomic Orbitals for Molecular Orbitals (LCAO-MO)
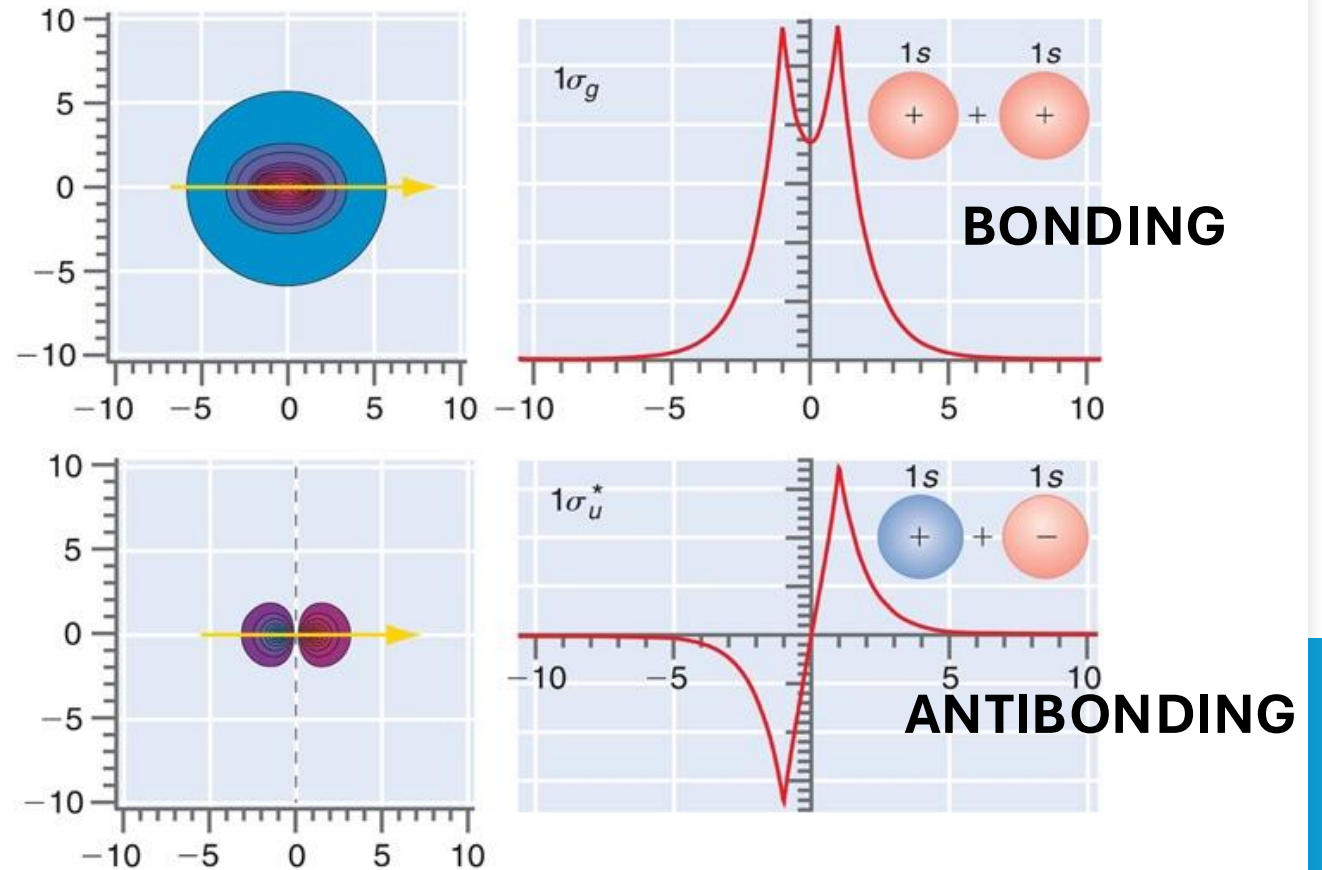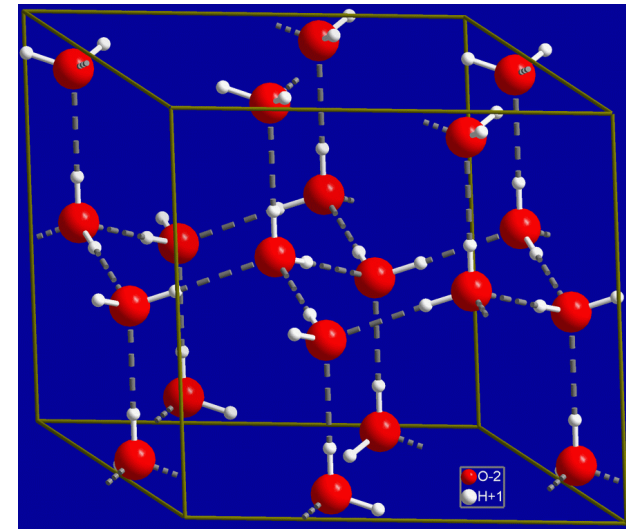
Intermolecular Forces

Orders of magnitudes smaller than typical chemical bonds

- Coulomb interactions
- Polarization/Induction: e.g., dipole-dipole interactions between polar molecules
- Dispersion/Van der Waals: e.g., induced dipole-induced dipole interactions
- Exchange repulsion: a purely quantum mechanical effects

Hydrogen Bond
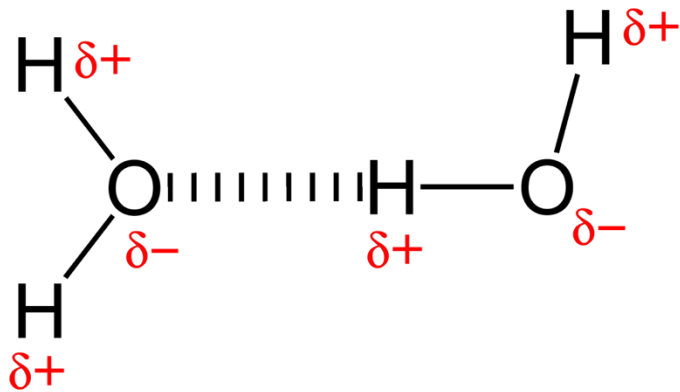
Ab Initial Quantum Chemistry Methods

- Computational techniques that are based on quantum chemistry that aim to solve the electronic SE.
- *Ab initio:* "from first principles", only use physical constants and positions of electrons etc as input.
- Increased sophistication of methods to approach exact solution to the electronic Schrödinger equation
- Formal scaling of methods based on system size, *N (e.g., number of basis functions)*

Scaling Behavior	Method	
N^4	Hartree-Fock (HF), hybrid Density Function Theory (DFT)	Up to ~1000 atoms
N^5	Møller-Plesset Second-Order Perturbation Theory (MP2)	Up to ~ 100 atoms
N^7	Coupled-Cluster with Singles and Doubles and Perturbative Triples excitations (CCSD(T))	Up to ~ 10-20 atoms
N^8	Coupled-Cluster with Singles and Doubles and Triples excitations (CCSDT)	< 10 atoms
$N!$	Full Configuration-Interaction (Full-CI)	Diatomics

Exact Solution ↓

Dynamic correlation required to capture weak non-covalent interactions like van der Waals
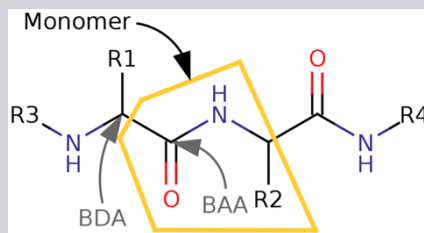
Fragmentation Methods

Effective fragment potential (EFP)

- A QM-based force field
- Designed to model solvent effects
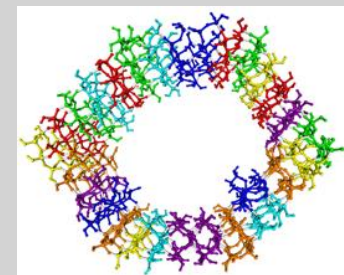- Noncovalent interactions
- Internally Rigid fragments
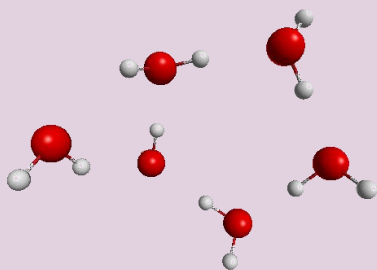
Fragment molecular orbital (FMO)

- partition system into smaller pieces
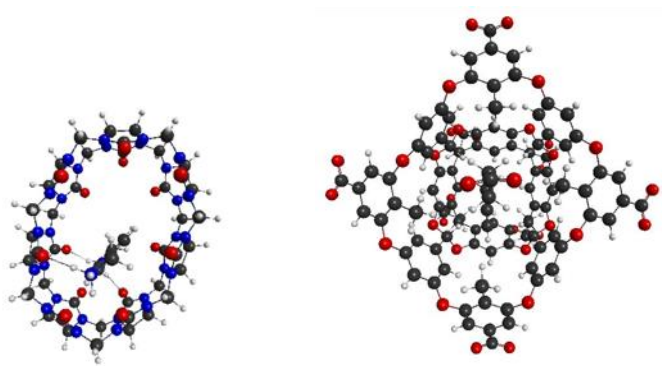- Ab initio method based on many-body expansion
- Flexible fragments

Effective fragment molecular orbital (EFMO)

- Merger of EFP and FMO
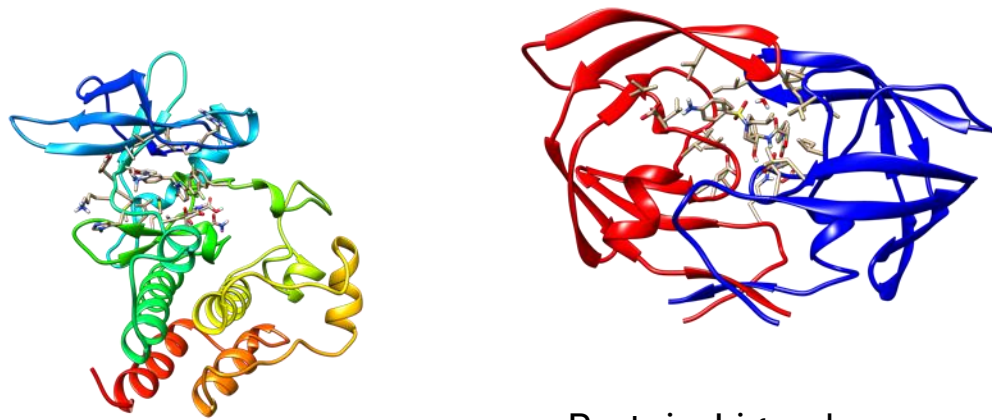- Simplifies FMO and improves accuracy
- Ab initio method
- Flexible fragments

$$E \cong \sum_{I}^{n_F} E_I \ + \sum_{I<J}^{n_F} \Delta E_{IJ} + \sum_{I<J<K}^{n_F} \Delta E_{IJK} + \cdots$$
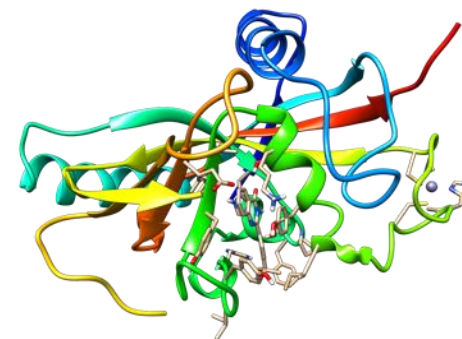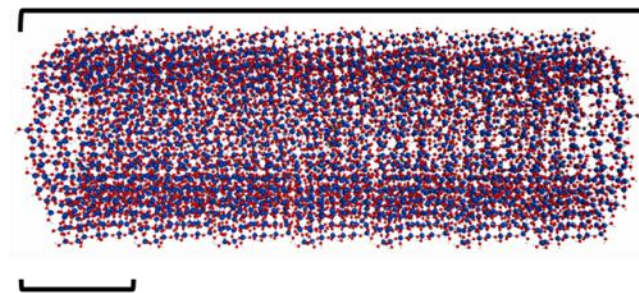
Applications of Quantum Chemistry
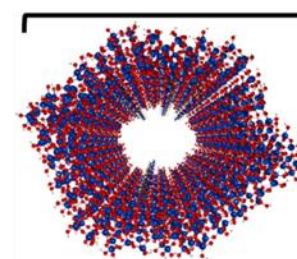

Host-Guest

Protein-Ligand

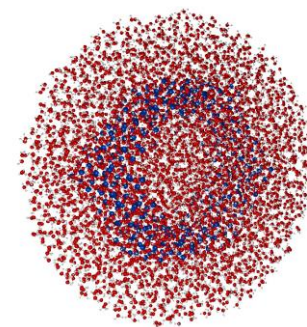~140 Angstroms (extended system, 12166 atoms)

~56 Angstroms

Solvated

~20 Angstroms

Mesoporous silica nanoparticles (MSNs)

Summary

$$\widehat{H}\Psi(\boldsymbol{r}) = E\Psi(\boldsymbol{r})$$