Lecture 1:
Basics of Quantum Chemistry

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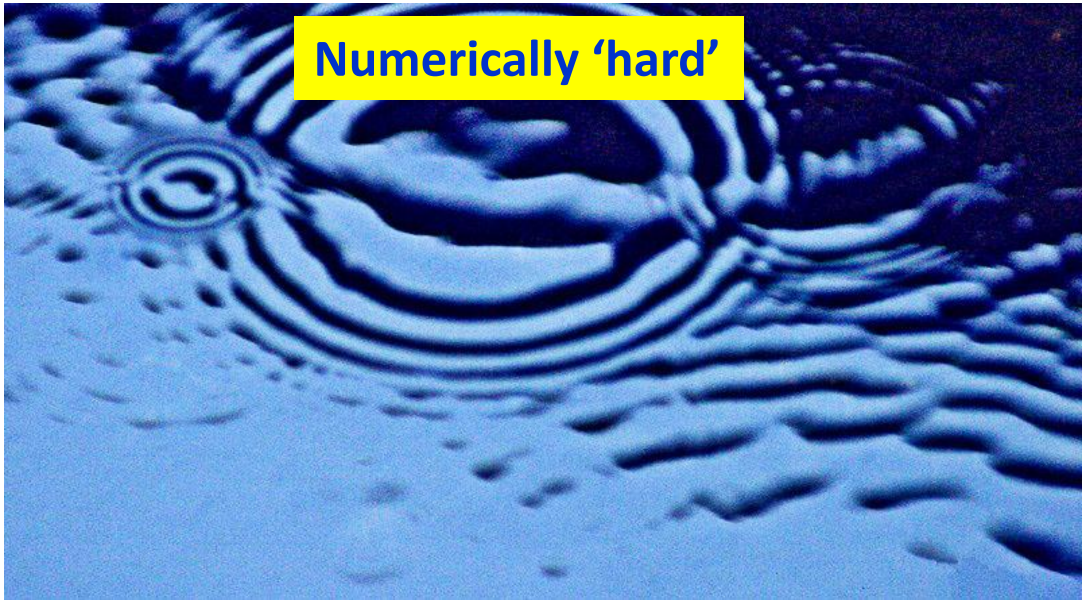
Computational Chemistry and Materials Modeling

Skoltech

Outline

- Basics of quantum mechanics
  - Schrödinger equation
  - Models
- Basics of quantum chemistry
  - Born-Oppenheimer approximation
  - Electronic structure problem: overview
  - Basis sets

We are going to quantum world!



It's the mechanics of waves, instead of classical particles. Description of the wave: amplitude (with phase) at every moment. $\Psi = \Psi(\vec{r}, t)$

Newtonian equation for quantum objects is time-dependent Schrödinger's equation

$$i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r},t) + V(\mathbf{r})\psi(\mathbf{r},t)$$

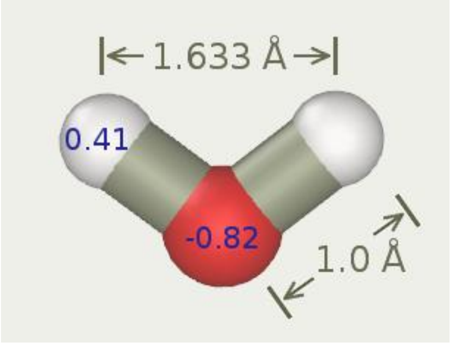
Classical system of particles described by Newtonian equation of motion $\mathbf{F} = m\mathbf{a}$

When do we need quantum mechanics?

***Materials** (atoms, molecules, nanostructures, solids) = electrons + nuclei,* $m_e \ll M_N$

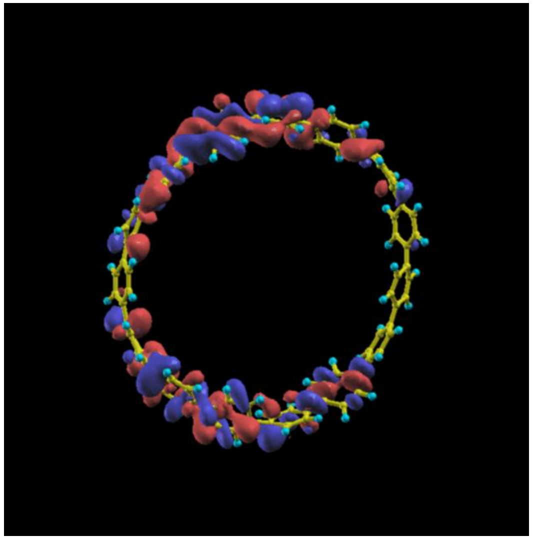
Electrons do require quantum description in most cases: stationary state, evolution, charge density distribution, electric and magnetic properties, spectroscopic/optical properties (interaction with light) etc.

Partial charges on the water



Nuclei do NOT require quantum description in most cases (classical framework is sufficient). However, quantum mechanics becomes important for specific phenomena such as vibrational (generally vibronic) spectroscopy, tunneling, non-adiabatic electron-vibrational dynamics etc.

Evolution of the light-induced electronic density during excited state dynamics

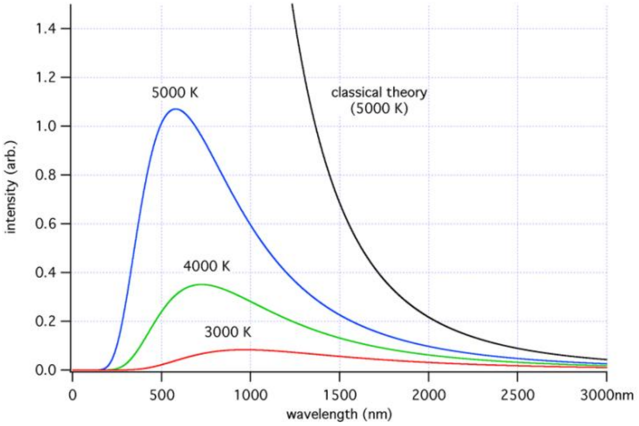


Light: Usually, for interaction of materials with light (electromagnetic field), Maxwell's classical theory (Maxwell equations) suffices. Simple particle model (photon) is necessary for spectroscopic modeling.

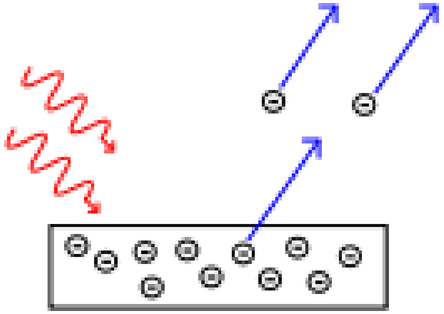
Historical motivations for quantum mechanics

1) *The ultraviolet catastrophe:* the blackbody radiation described by the Rayleigh-Jeans law $B_\nu(T) = \frac{2\nu^2 kT}{c^2}$ diverges for short wavelength.

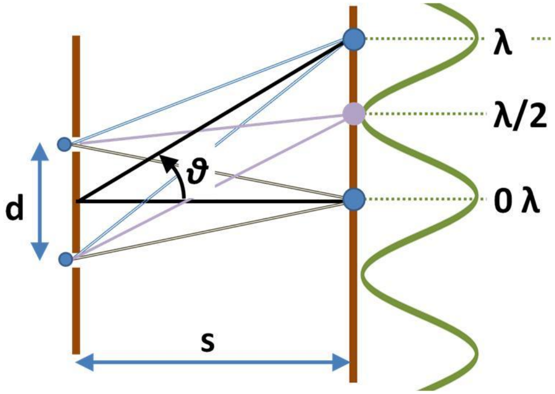
Max Planck in 1900 assumed quantized energies of electronic oscillations giving rise to the emission of radiation $E = nh\nu$ which explained the blackbody radiation.



2) *The photoelectric effect:* Heinrich Hertz (1887) discovered that ultraviolet light can cause electrons to be ejected from a metal surface AND the kinetic energy of the ejected electrons depends on the *frequency* (not on intensity) of the light. Einstein (1905) assumed quantized nature of radiation itself $E = h\nu$
Einstein (1907) proved quantized atomic vibrations.



3) *Double slit experiments:* De Broglie (1924) argued that matter also can exhibit this *wave-particle duality*. Experimental confirmation: Davisson and Germer (1927) observed electronic diffraction patterns by bombarding metals with electrons.



The Schrödinger Equation

__1925:__ The first (and independent) formulation of quantum theory by __Erwin Schrödinger__ (partial differential equations) and __Werner Heisenberg__ (matrix formulation)

Time-independent Schrödinger equation for a particle/wave with mass m in potential V

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

or

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$$

Time-dependent Schrödinger equation for a single particle/wave

$$i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r},t) + V(\mathbf{r})\psi(\mathbf{r},t)$$

The Schrödinger equation provides a way to calculate the possible wave functions of a system and how they dynamically change in time. However, the Schrödinger equation does not directly say *what*, exactly, the wave function is. But: it is consistent with energy conservation, linear and consistent with De Broglie relations!

Operators and Quantum Mechanics

An operator is a rule that transforms a given function into another function (common definition, e.g., by Levine)

The Hamiltonian operator $\hat{H} = -\frac{\hbar^2}{2}\sum_i \frac{1}{m_i}\nabla_i^2 + V$ $\quad i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi$

Also the expectation value of any operator A: $< A >= \int \psi^*(\mathbf{r})\hat{A}\psi(\mathbf{r})d\mathbf{r}$

The sum and product of two operators: $(\hat{A}+\hat{B})f \;=\; \hat{A}f + \hat{B}f \qquad \hat{A}\hat{B}f \equiv \hat{A}[\hat{B}f]$

A complete set of states and identity operator $\sum_i |i\rangle\langle i|f = \hat{1}f = f$

Function of the operator: Taylor series + the n-th power of an operator, e.g. $\hat{A}^2 f = \hat{A}\hat{A}f$ allow to define any function of the operator, for example, the exponential

$$e^{\hat{A}} = \hat{1} + \hat{A} + \frac{\hat{A}^2}{2!} + \frac{\hat{A}^3}{3!} + \cdots$$

The associative law is valid for operators: $\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C}$

The commutative law : $[\hat{A},\hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$ In general: $\hat{A}\hat{B} \neq \hat{B}\hat{A}$

Some basic properties of the operators

Linear operators

$$\begin{aligned}\hat{A}(f+g) &= \hat{A}f + \hat{A}g \\ \hat{A}(cf) &= c\hat{A}f\end{aligned}$$

Eigenstate (eigenfunction+eigenvalue) of the operator

If $\hat{A}\psi(\mathbf{r}) = a\psi(\mathbf{r})$

$$< A > \; = \int \psi^*(\mathbf{r})\hat{A}\psi(\mathbf{r})d\mathbf{r} = \; a$$

Hermitian operator $\hat{A} = \hat{A}^\dagger$

$$\int \psi^*(\mathbf{r})\hat{A}\psi(\mathbf{r})d\mathbf{r} = \int (\hat{A}\psi(\mathbf{r}))^*\psi(\mathbf{r})d\mathbf{r}$$

1) Eigenvalues are real;
2) Eigenvectors can be chosen to be orthogonal;
3) Corresponds to a symmetric matrix

Unitary operator (useful for transformation from one representation to another)

$$U^{-1} = U^\dagger$$

$$UU^\dagger = U^\dagger U = I$$

Commutators :

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

$$[\hat{A}, \hat{B}] + [\hat{B}, \hat{A}] = 0$$

If $[\hat{A}, \hat{B}] = i\hat{C}$ then $(\Delta A)(\Delta B) \geq \frac{1}{2}| < C > |$

$$[\hat{A}, \hat{A}] = 0$$

$$(\Delta x)(\Delta p_x) \geq \frac{\hbar}{2}$$

$$\Delta A^2 = < A^2 > - < A >^2$$

$$[\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}]$$

$$[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$$

$$e^{\hat{A}}\hat{B}e^{-\hat{A}} = \hat{B} + [\hat{A}, \hat{B}] + \frac{1}{2!}[\hat{A}, [\hat{A}, \hat{B}]] + \frac{1}{3!}[\hat{A}, [\hat{A}, [\hat{A}, \hat{B}]]] + \cdots$$

Heisenberg uncertainty principle

$$(\Delta x)(\Delta p_x) \geq \frac{\hbar}{2}$$

Quantum Mechanics and linear vector spaces

Most operators in quantum mechanics are linear operators -> allows representation of quantum mechanical operators as matrices and wavefunctions as vectors in some linear vector space. Great for numerical calculations!

Assuming orthonormal $(\hat{\Psi}_i, \hat{\Psi}_j) = \delta_{ij}$ and complete basis set, any $\Psi = \sum_{i=1}^{n} a_i \Psi_i$

Or vector notation for Dirac's "ket-" and "bra-" $|\Psi_a\rangle = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix}$ $\langle \Psi_a| = (a_1^* a_2^* \cdots a_n^*)$

The scalar product:

$$\langle \Psi_a | \Psi_b \rangle = \int \Psi_a^*(x) \Psi_b(x) dx = \left(\sum_i a_i \hat{\Psi}_i, \sum_j b_j \hat{\Psi}_j\right) = \sum_i a_i^* b_i = (a_1^* a_2^* \cdots a_n^*) \begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ b_n \end{pmatrix}$$

And finally an operator is defined by a matrix: $\hat{A}\hat{\Psi}_j = \Psi'_j = \sum_i^n \hat{\Psi}_i A_{ij}$ $A_{ij} = \langle i | \hat{A} | j \rangle$

So that $\Psi_b = \hat{A}\Psi_a$ is represented as

$$\begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ b_n \end{pmatrix} = \begin{pmatrix} A_{11} & A_{12} & \cdots & A_{1n} \\ A_{21} & A_{22} & \cdots & A_{2n} \\ \vdots & \vdots & & \vdots \\ A_{n1} & A_{n2} & \cdots & A_{nn} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix}$$

For Hermitian operator

$$A_{ji}^* = A_{ij}^\dagger$$

Foundational principles of QM

(following C. D. Sherrill, GaTech)

1) The wavefunction $\Psi(\mathbf{r},t)$ completely specifies the state of a quantum mechanical system that depends on the coordinates of the particle(s) and on time.

2) Wavefunction (= probabilistic interpretation) with normalization

$$\int_{-\infty}^{\infty} \Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t)d\tau = 1$$

3) To every observable in classical mechanics there is a corresponding linear and Hermitian operator in quantum mechanics

Observable Name	Observable Symbol	Operator Symbol	Operator Operation
Position	$\mathbf{r}$	$\hat{\mathbf{r}}$	Multiply by $\mathbf{r}$
Momentum	$\mathbf{p}$	$\hat{\mathbf{p}}$	$-i\hbar\left(\hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}\right)$
Kinetic energy	T	$\hat{T}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$
Potential energy	$V(\mathbf{r})$	$\hat{V}(\mathbf{r})$	Multiply by $V(\mathbf{r})$

4) Experimental measurements are associated with eigenvalues a, satisfying the eigenvalue equation.

$$\hat{A}\Psi = a\Psi$$

Even for superposition of states

$$\Psi = \sum_i^n c_i \Psi_i$$

5) An average value of the observable: $< A >= \int \psi^*(\mathbf{r})\hat{A}\psi(\mathbf{r})d\mathbf{r}$

6) The wavefunction obeys the time-dependent Schrödinger equation: $\hat{H}\Psi(\mathbf{r},t) = i\hbar\frac{\partial\Psi}{\partial t}$

7) In the case of fermions, the wavefunction has to be antisymmetric with respect to the interchange of all coordinates of two particles

The Schrödinger cat

Experimental measurements are associated with eigenvalues a, satisfying the eigenvalue equation.

Even for superposition of states

$$\hat{A}\Psi = a\Psi \qquad \Psi = \sum_{i}^{n} c_i \Psi_i$$

Schrödinger's cat is a thought experiment, a hypothetical cat that may be simultaneously both alive and dead, a state known as a quantum superposition

The variational method

We do not know an exact wavefunction, but what can we say about any trial wavefunction?

The variational principle

$$\frac{\int \Phi H \Phi d\mathbf{r}}{\int \Phi^2 d\mathbf{r}} \geq E_0$$

In a search for the best wavefunction to define the ground state of a system, the quality of the guess wave functions can be evaluated by their associated energies: *the lower is the better*!

Proof

$\Phi = \sum_i c_i \Psi_i$ where Ψ_i are the eigenfunctions of $H\Psi = E\Psi$

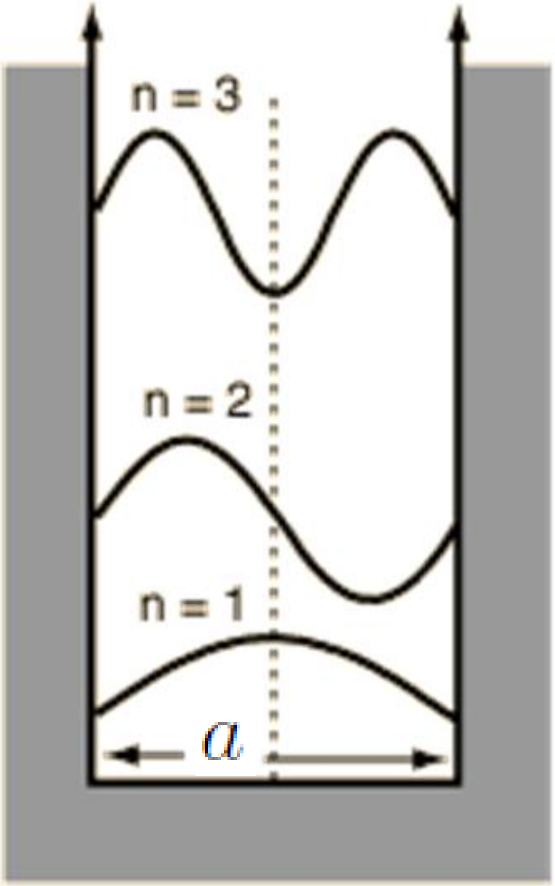
Normalization $\int \Phi^2 d\mathbf{r} = 1 = \int \sum_i c_i \Psi_i \sum_j c_j \Psi_j d\mathbf{r} = \sum_{ij} c_i c_j \int \Psi_i \Psi_j d\mathbf{r} = \sum_i c_i^2$

Expectation value $\int \Phi H \Phi d\mathbf{r} = \int \left(\sum_i c_i \Psi_i\right) H \left(\sum_j c_j \Psi_j\right) d\mathbf{r} = \sum_{ij} c_i c_j \int \Psi_i H \Psi_j d\mathbf{r} = \sum_i c_i^2 E_i$

If ground state is (E_0 and Ψ_0) than $\int \Phi H \Phi d\mathbf{r} - E_0 \int \Phi^2 d\mathbf{r} = \sum_i c_i^2 (E_i - E_0) \geq 0$

Illustration 1: The Particle in a Box

A particle constrained to move in a single dimension, under the in influence of a potential V (x) which is zero for 0 < x <a and infinite elsewhere.



x = 0 at left wall of box.

The Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi(x) \quad 0 \leq x \leq a$$

Boundary conditions: $\psi(x)$ is zero at x=0 and *a*

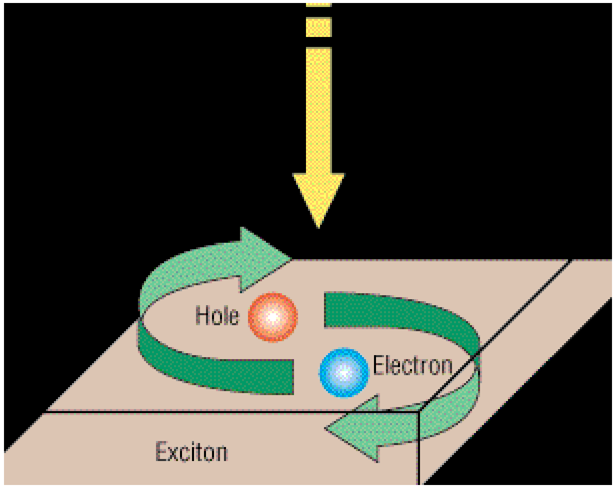
Solution

$$\psi_n(x) = \sqrt{\frac{2}{a}} sin\left(\frac{n\pi x}{a}\right) \qquad 0 \leq x \leq a \qquad n = 1, 2, 3, \ldots$$

$$E_n = \frac{h^2 n^2}{8ma^2} \qquad n = 1, 2, \ldots$$

Note existence of the quantum number and oscillating nature of the wavefunctions (standing waves), where the number of nodes is related to the quantum number

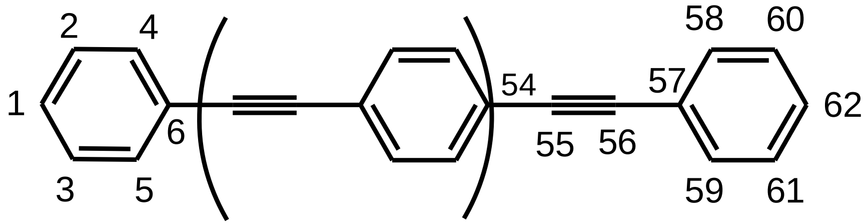
Case study 1: Excitons on the molecule



Binding energy (Coulomb e-h interaction)

$$V(r) = -\frac{e^2}{\varepsilon}\int dz_e \int dz_h \frac{|\psi_e(z_e)|^2|\psi_h(z_h)|^2}{[r^2+(z_e-z_h)^2]^{1/2}}.$$

Particle (exciton) is in a box



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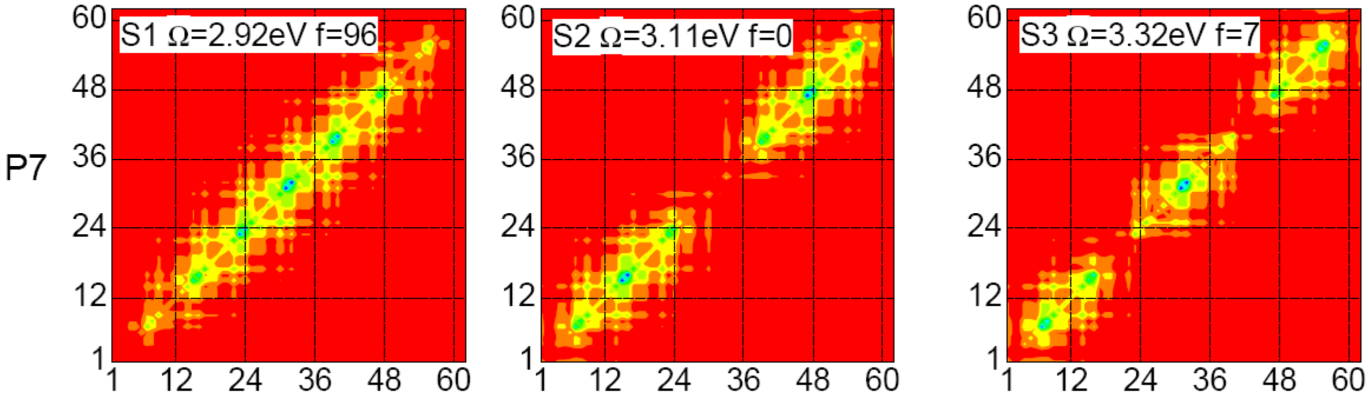
Enhanced e-h interactions can be due to small dielectric constant and low-dimensionality



State 1 **State 2** **State 3**

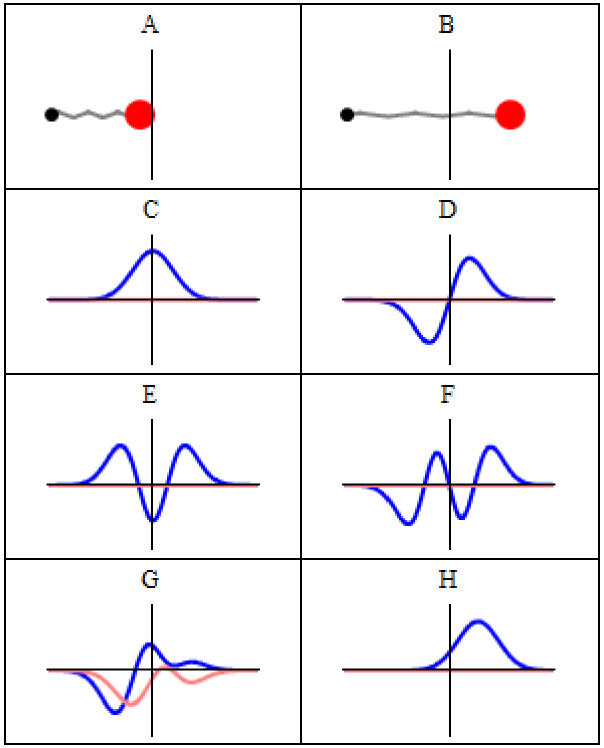
C. Wu, S. Malinin, S. Tretiak, and V. Chernyak, Nature Phys., 2, 631 (2006)

Illustration 2: The Harmonic Oscillator

A particle subject to a restoring force (e.g. Hooke's Law)

$F = -kx$ ***i.e., a potential*** $V(x) = (1/2)kx^2$ ***Applies to a single particle or 2 particles with reduced mass*** μ

The Schrödinger equation $-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi(x) = E\psi(x)$



Solution

$$\psi_n(x) = N_n H_n(\alpha^{1/2}x)e^{-\alpha x^2/2} \qquad n = 0, 1, 2, \ldots$$

$$\alpha = \sqrt{\frac{k\mu}{\hbar^2}} \qquad N_n = \frac{1}{\sqrt{2^n n!}}\left(\frac{\alpha}{\pi}\right)^{1/4}$$

H_n the Hermite polynomial of degree *n*

Energy levels:

$$E_n = \hbar\omega(n + 1/2)$$

$$\omega = \sqrt{k/\mu}$$

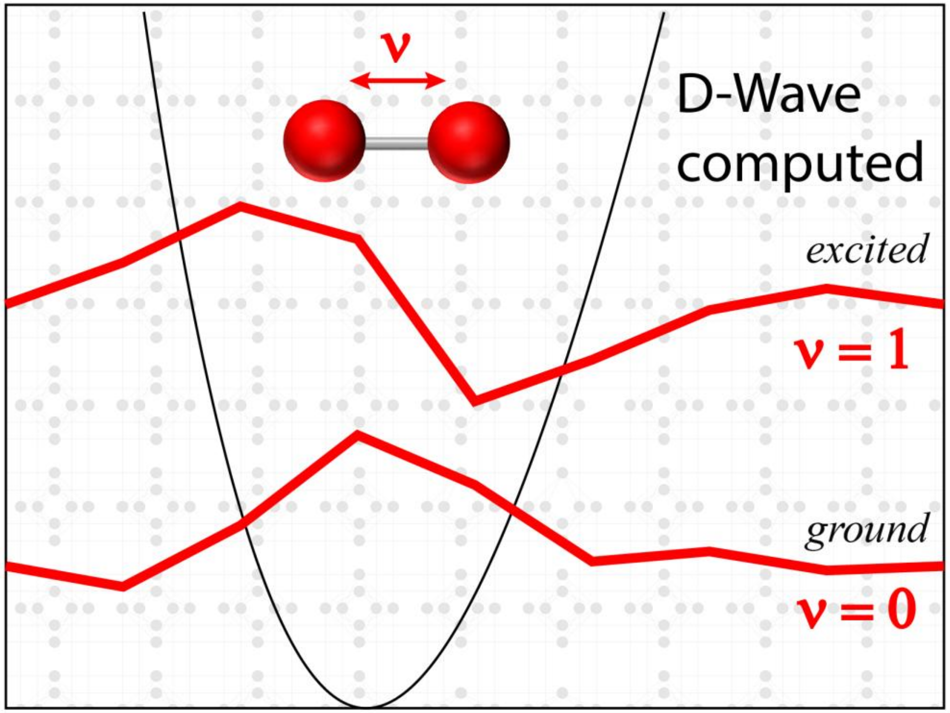
This model is foundational for ALL vibronic spectroscopy!!!!

Wikipedia: Some trajectories of a harmonic oscillator (i.e. a ball attached to a spring) in classical mechanics (A-B) and quantum mechanics (C-H). In quantum mechanics, the position of the ball is represented by a wave (wavefunction), with the real part shown in blue and the imaginary part shown in red. Some of the trajectories (such as C,D,E,and F) are standing waves (or "stationary states"). Each standing-wave frequency is proportional to a possible energy level of the oscillator. (G-H) are non-stationary states (G) is a randomly-generated superposition of the four states (C-F). H is a "coherent state" which somewhat resembles the classical state B.

Case study 2: The Harmonic Oscillator solved on quantum computer (D-wave)

The Quantum Computing Company™

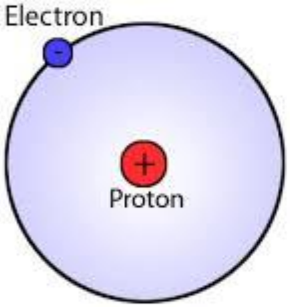
The quantum annealer eigensolver (QAE) is developed and applied to compute the vibrational spectrum of a molecule on LANL's D-Wave machine "Ising". The D-Wave computed ground and first excited state vibrational wave functions of O_2 are plotted in red. The attractive interaction potential between the two oxygen atoms (red spheres) is plotted in black. The vibrational state is labeled by the quantum number ν where ν=0 is the ground state and ν=1 is the first excited state.



D-Wave 2X computer, with 1000 qubits. 'Advantage' QAE architecture is coming

A. Teplukhin, B. K. Kendrick, and D. Babikov, J. Chem. Theory Comput. 15 4555 (2019)

Illustration 3: The Hydrogen Atom



A proton fixed at the origin is orbited by an electron of reduced mass μ

The Coulomb potential and the kinetic energy:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \qquad \hat{T} = -\frac{\hbar^2}{2\mu}\nabla^2$$

The Schrödinger equation in spherical polar coordinates

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)\frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2 sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]-\frac{e^2}{4\pi\epsilon_0 r}\psi(r,\theta,\phi)=E\psi(r,\theta,\phi)$$

The radial and angular parts are separable $R(r)_{nl}Y_l^m(\theta,\phi)$

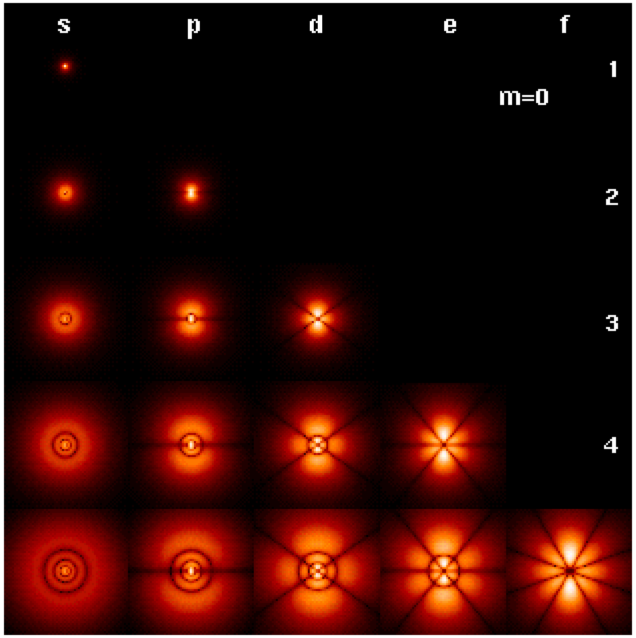
$$-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{\hbar^2 l(l+1)}{2\mu r^2}+V(r)-E\right]R(r)=0$$

Solutions: Radial part via the Laguerre functions and angular part via the spherical harmonics

Energy levels: $$E_n = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2} \qquad n = 1, 2, \ldots$$

Quantum numbers:

$$n = 1, 2, 3, \ldots$$
$$m = -\ell, \ldots, \ell.$$
$$\ell = 0, 1, 2, \ldots, n-1$$



Wikipedia: Probability densities for the electron at different quantum numbers (ℓ, n, m = 0)

Illustration 3: The Hydrogen Atom

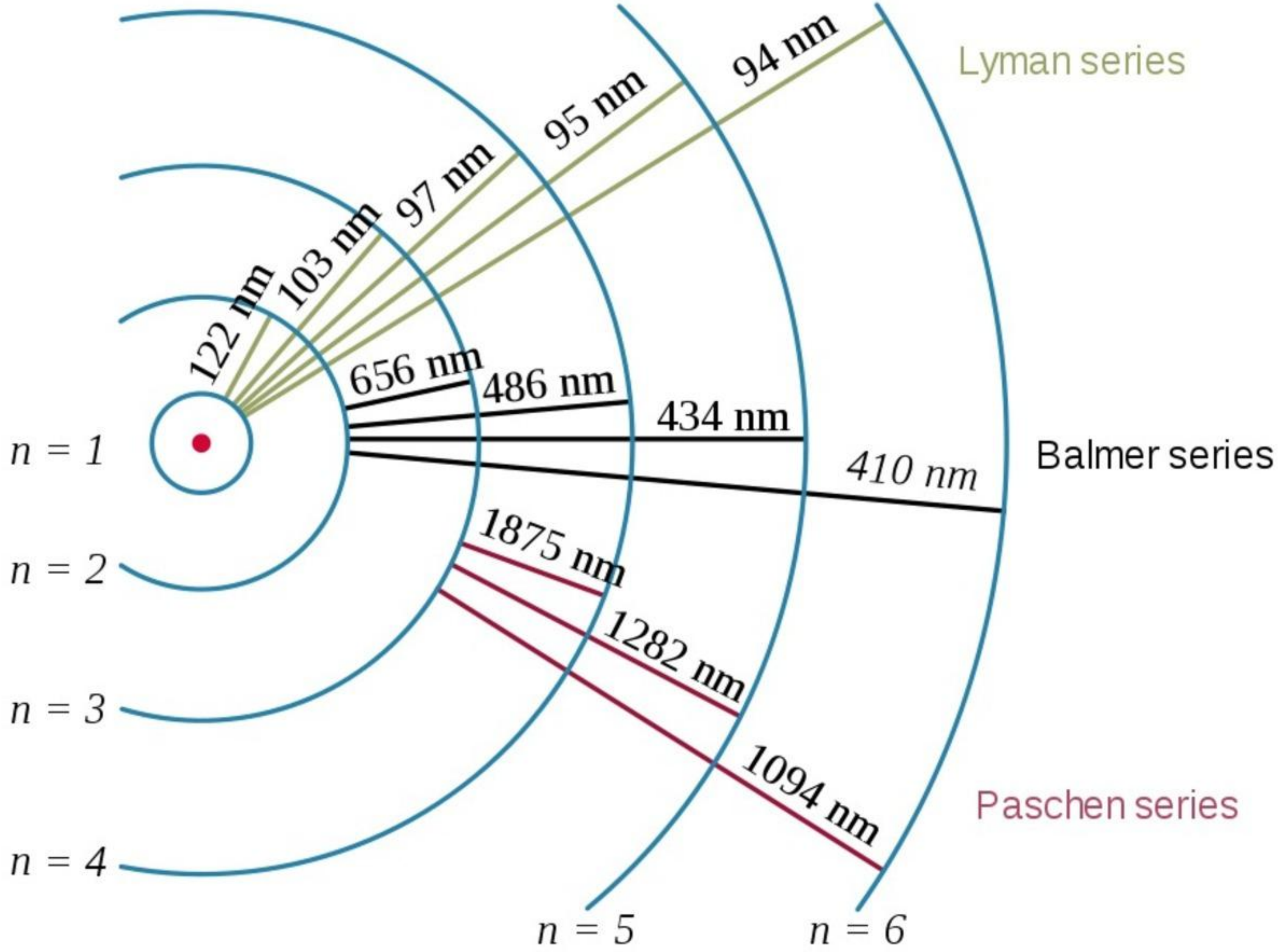
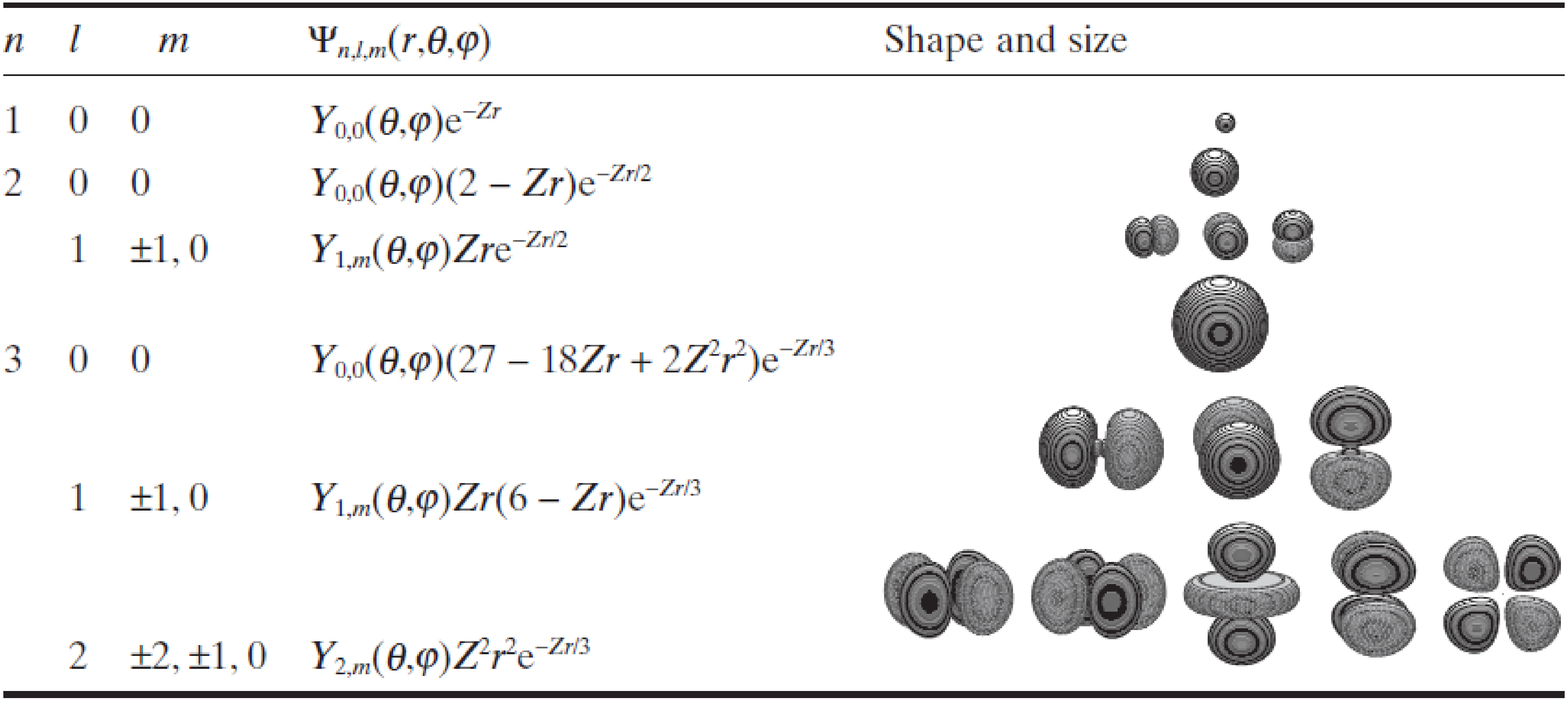


Illustration 3: The Hydrogen Atom

Three *quantum numbers*, *n*, *l* and *m* correspond to the three spatial variables **r**, θ and φ. The *n* quantum number describes the *size* of the orbital, the *l* quantum number describes the *shape* of the orbital, while the *m* quantum number describes the *orientation* of the orbital.

$l = 0$: s-orbital
$l = 1$: p-orbital
$l = 2$: d-orbital

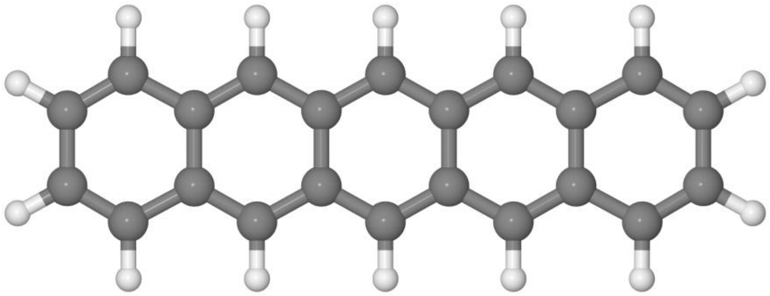
Table 1.2 Hydrogenic orbitals obtained from solving the Schrödinger equation (from Jensen)

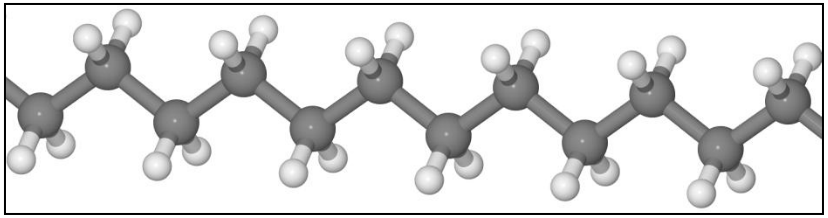


n	l	m	$\Psi_{n,l,m}(r,\theta,\varphi)$	Shape and size
1	0	0	$Y_{0,0}(\theta,\varphi)e^{-Zr}$	
2	0	0	$Y_{0,0}(\theta,\varphi)(2-Zr)e^{-Zr/2}$	
	1	±1, 0	$Y_{1,m}(\theta,\varphi)Zre^{-Zr/2}$	
3	0	0	$Y_{0,0}(\theta,\varphi)(27-18Zr+2Z^2r^2)e^{-Zr/3}$	
	1	±1, 0	$Y_{1,m}(\theta,\varphi)Zr(6-Zr)e^{-Zr/3}$	
	2	±2, ±1, 0	$Y_{2,m}(\theta,\varphi)Z^2r^2e^{-Zr/3}$	

Quantum mechanics models

- Free particle
- Particle in a box
- Harmonic oscillator
- Hydrogen atom
- Kronig-Penney model
- Tight-binding models





Discussion

1. **By examining wavefunctions for solution of particle in a box problem, harmonic oscillator or hydrogen atom, what are the common features? Why?**

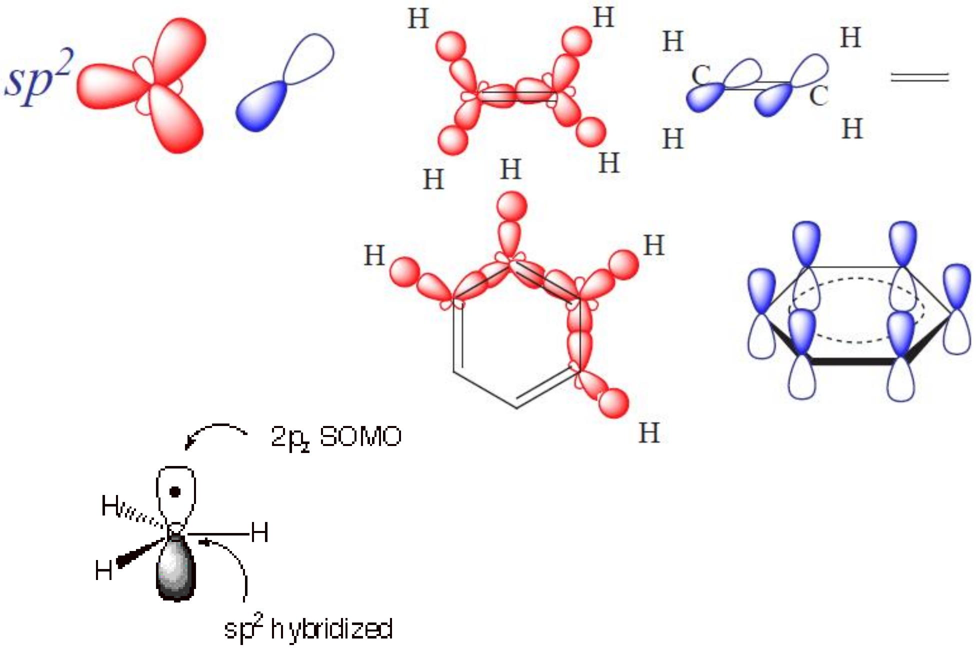
2. **Solving Schrödinger equation scale exponentially with the number of particles. Why?**

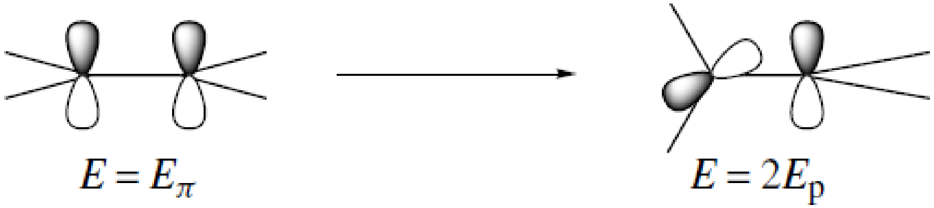
3. **Why does mapping linear operators of quantum mechanics into linear algebra advantageous for numerical solutions?**

Simple approach: The Hückel approximation

An example of tight-binding Hamiltonian, first constructed by Erich Huckel in 1930-1931 for aromatic hydrocarbons

1) Only π –orbitals (one per carbon, the blue color) are considered
2) The orbitals are orthogonal $\mathbf{S}_{ij} = \delta_{ij}$
3) Diagonal resonance term $\boldsymbol{H_{ii}=\alpha}$ is derived from the ionization potential of methyl radical.
4) Off-diagonal nearest neighbor resonance terms are also derived from experimental data: $\boldsymbol{E_p=\alpha}$ and $\boldsymbol{E_\pi=\alpha+2\beta}$
5) Not nearest-neighbor resonance interactions are neglected!





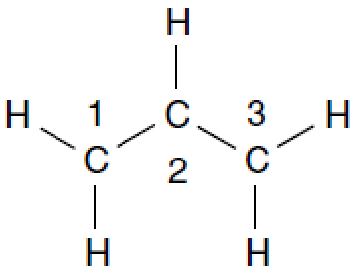
Provides simplified but conceptually very attractive Hamiltonian model!

Hückel approach to hydrocarbons

The allyl system, following Cramer

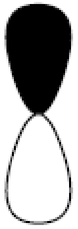
The secular equation:

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0$$



Eigenvalues correspond to bonding, non-bonding and anti-bonding molecular orbitals:

$$E = \alpha + \sqrt{2}\beta, \quad \alpha, \quad \alpha - \sqrt{2}\beta$$



p_C

The bonding (lowest energy) MO

$$\varphi_1 = \frac{1}{2}p_1 + \frac{\sqrt{2}}{2}p_2 + \frac{1}{2}p_3$$

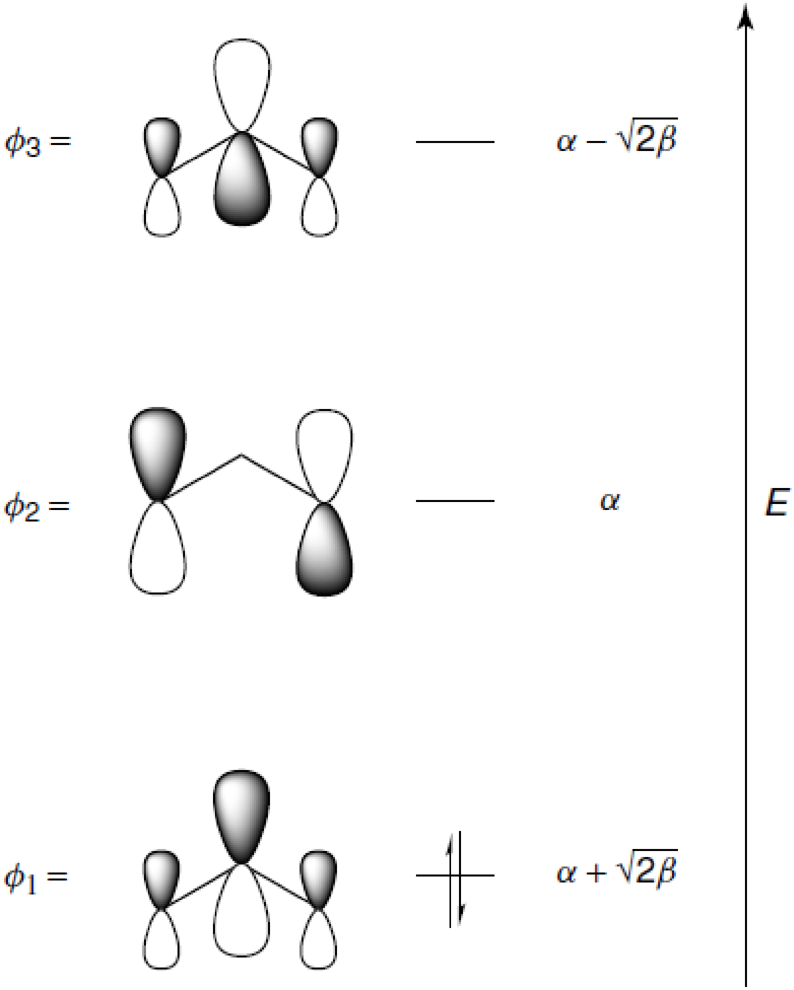


Figure 4.2 from Cramer: Huckel MOs for the allyl system

2 electrons per orbital starting from the bottom!

π –bonding energy of the system:

allyl cation (2e) $2(\alpha + \sqrt{2}\beta)$

allyl radical (3e) $2(\alpha + \sqrt{2}\beta) + \alpha$

allyl anion (4e) $2(\alpha + \sqrt{2}\beta) + 2\alpha$

Case study 3: Extended Hückel Theory with Machine Learning

Extended Hückel theory is one of the simplest methods for simulating the electronic structure of molecules.

Hamiltonian form:

$$H_{ij} = \frac{1.75}{2}(H_i + H_j)S_{ij}$$

$$H_{carbon,\,s} = -21.4\ eV;\ H_{carbon,\,P} = -11.4\ eV;\ H_{hydrogen,\,s} = -13.6\ eV$$

Solve the Schrodinger equation:

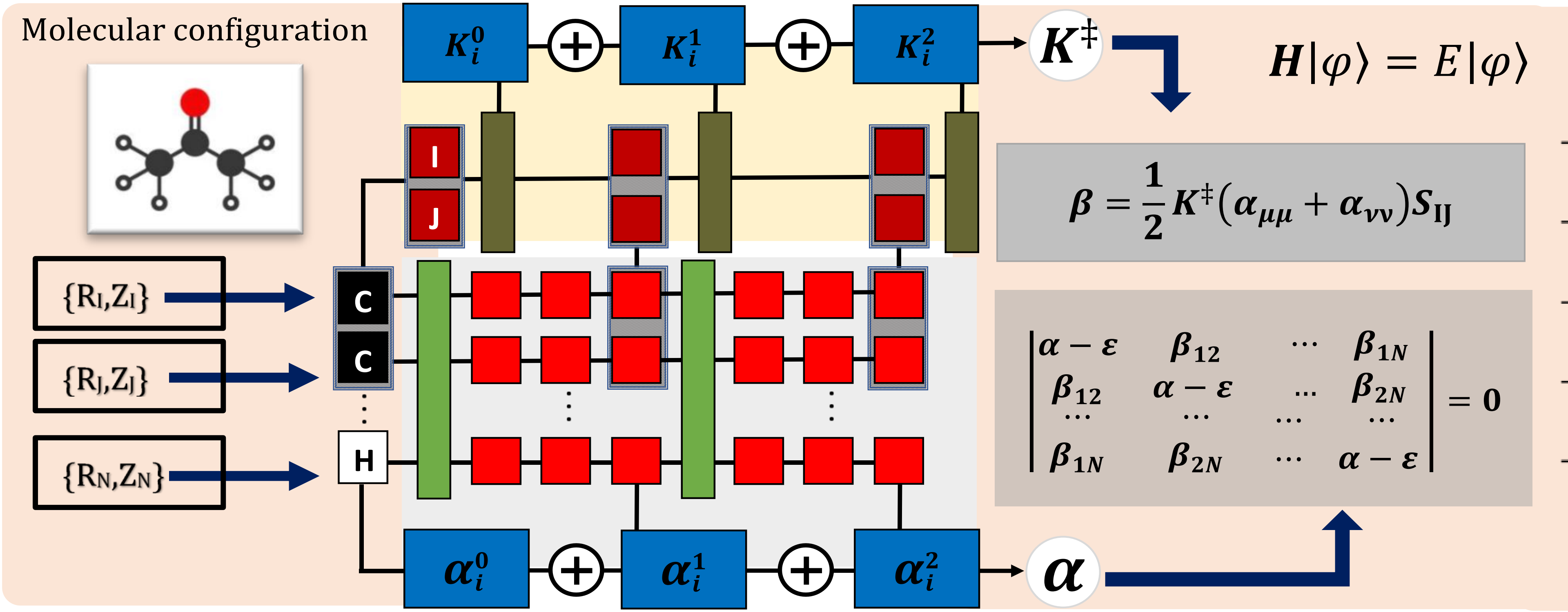
$$H\psi = ES\psi$$

Can we optimize the Hamiltonian parameters to match DFT eigenvalues and energies?

ML-scheme for learning Hückel Hamiltonians

Hierarchically Interacting Particle Neural Network

ML Effective Hamiltonian



$$H|\varphi\rangle = E|\varphi\rangle$$

$$\beta = \frac{1}{2}K^\ddagger(\alpha_{\mu\mu} + \alpha_{\nu\nu})S_{IJ}$$

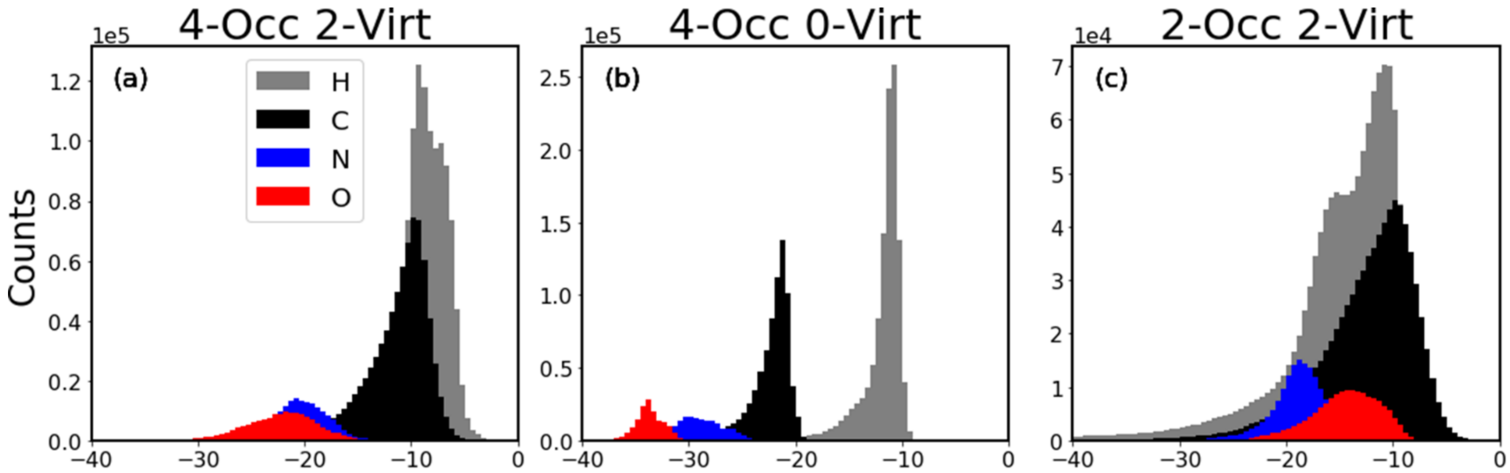
$$\begin{vmatrix} \alpha-\varepsilon & \beta_{12} & \cdots & \beta_{1N} \\ \beta_{12} & \alpha-\varepsilon & \cdots & \beta_{2N} \\ \cdots & \cdots & \cdots & \cdots \\ \beta_{1N} & \beta_{2N} & \cdots & \alpha-\varepsilon \end{vmatrix} = 0$$

Diagonal predictions that occur on each atom are used to parameterize the orbital energies. The layers (top) added to HIP-NN allow predictions off-diagonal Hamiltonian elements ($K^\ddagger$).

T. Zubatuk, B. Nebgen, Ni. Lubbers, J. S. Smith, R. Zubatuk, G. Zhou, C. Koh, K. Barros, O. Isayev, and S. Tretiak, *“Machine Learned Hückel Theory: Interfacing Physics and Deep Neural Networks”* J. Chem. Phys., **154**, 244108 (2021).

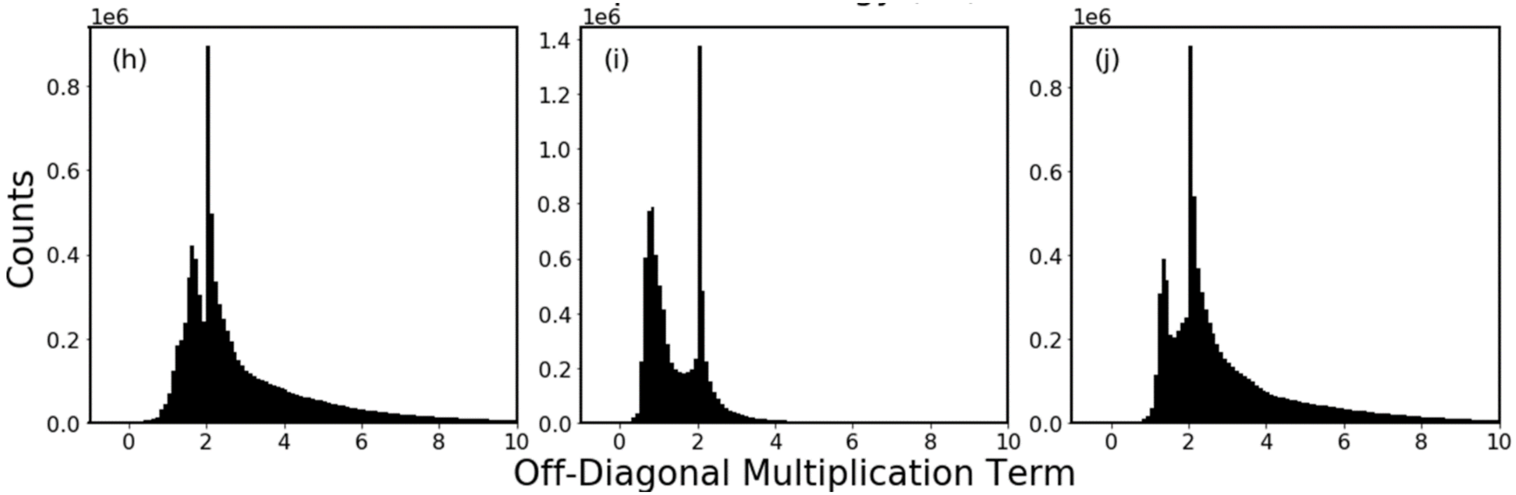
Is learned tight-binding model physical?

α



For 4-Occ 0-Virt" mode $\alpha_{H,s}$ orbital energy is -13.6 eV and O<N<C

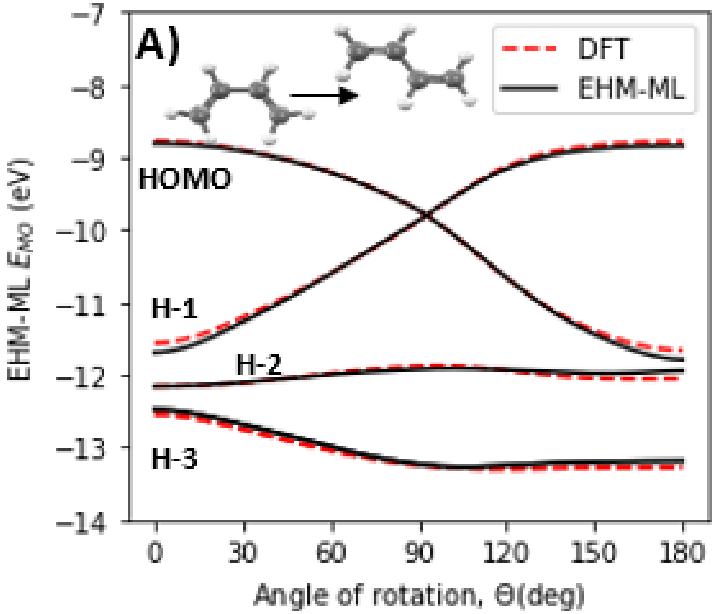
$K^\ddagger$

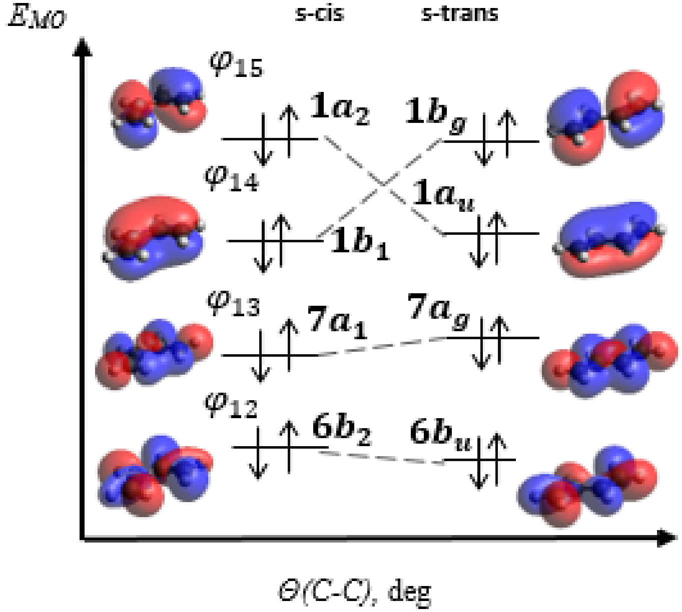


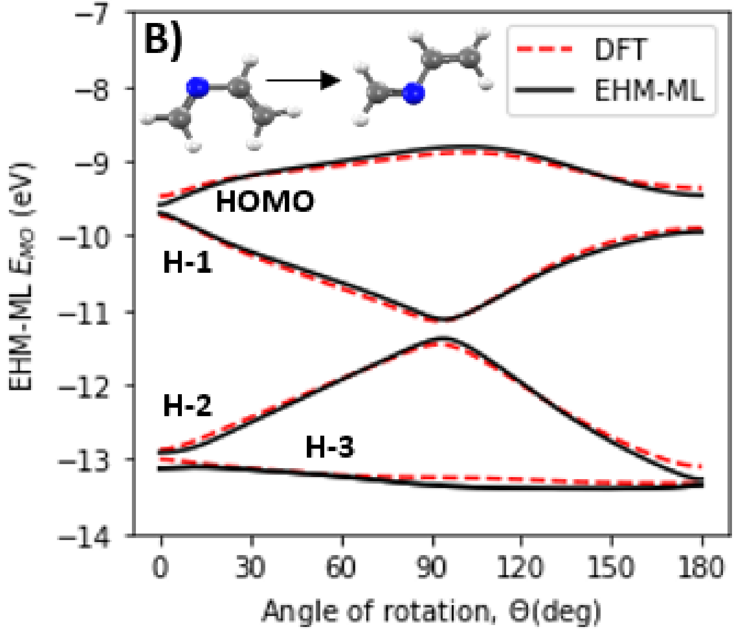
Distribution of $K^\ddagger$ has average of 1.5, close to original parameterization 1.75

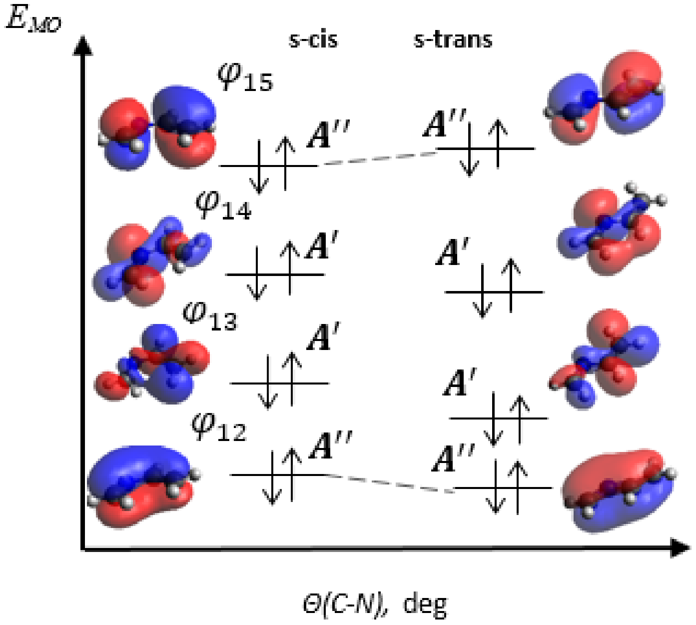
T. Zubatiuk, B. Nebgen, N. Lubbers, J. S. Smith, R. Zubatiuk, G. Zhou, C. Coh, K. Barros, O. Isayev, S. Tretiak, (2019) https://arxiv.org/abs/1909.12963

Reactions: butadiene and aza-butadiene









Quantum chemistry: molecular Hamiltonian

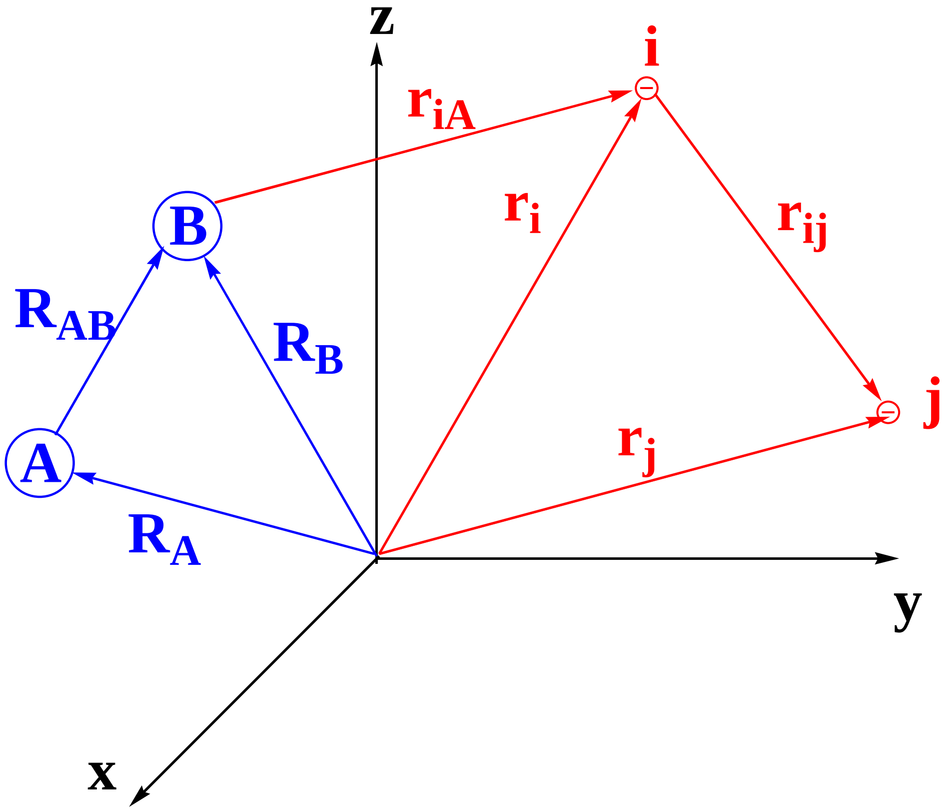
$$\hat{H} = -\sum_A \frac{1}{2M_A}\nabla_A^2 - \sum_i \frac{1}{2}\nabla_i^2 + \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} - \sum_{Ai} \frac{Z_A}{r_{Ai}} + \sum_{i>j} \frac{1}{r_{ij}}$$

OR

$$\hat{H} = \hat{T}_N(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{eN}(\mathbf{r},\mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$$

Exact nonrelativistic Hamiltonian in absence of external fields

(i.e. quantum system of particles interacting with Coulomb potential)



Atomic units (au) sets to be unity:

Electron mass m_e

Elementary charge e

Reduced Planck's constant $\hbar = h/(2\pi)$

Coulomb's constant $1/(4\pi\epsilon_0)$

What is neglected? Relativistic mass corrections (mostly inner electrons in heavy atoms), spin-orbit couplings (**L*S**)

The Born-Oppenheimer Approximation

Given separable Hamiltonian $\hat{H} = \hat{H}_1(q_1) + \hat{H}_2(q_2)$ ***for*** $\hat{H}\psi(q_1, q_2) = E\psi(q_1, q_2)$

Then $\psi(q_1, q_2) = \psi_1(q_1)\psi_2(q_2)$ ***(factorization) and*** $E = (E_1 + E_2)$ ***(additive)***

$$\hat{H} = \hat{T}_N(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{eN}(\mathbf{r}, \mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$$

Approximately separable! $\phi_T(\mathbf{r}, \mathbf{R}) = \phi_e(\mathbf{r}; \mathbf{R})\phi_N(\mathbf{R})$

$$\hat{H}\phi_e(\mathbf{r}; \mathbf{R})\phi_N(\mathbf{R}) = E_{tot}\phi_e(\mathbf{r}; \mathbf{R})\phi_N(\mathbf{R})$$

Electronic problem: $\hat{H}_e = \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}; \mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$

$$\hat{H}_e\phi_e(\mathbf{r}; \mathbf{R}) = \left\{-\frac{1}{2}\sum_i \nabla_i^2 - \sum_{A,i}\frac{Z_A}{r_{Ai}} + \sum_{i>j}\frac{1}{r_{ij}}\right\}\phi_e(\mathbf{r}; \mathbf{R}) = E_e(\mathbf{R})\phi_e(\mathbf{r}; \mathbf{R})$$

Nuclei problem: $\{\hat{T}_N + E_e + \hat{V}_{NN}\}\phi_N(\mathbf{R}) = E_{tot}\phi_N(\mathbf{R})$

$$\hat{H}_N\phi_N(\mathbf{R}) = \left\{-\sum_A \frac{1}{2M_A}\nabla_A^2 + E_e(\mathbf{R}) + \sum_{A>B}\frac{Z_A Z_B}{R_{AB}}\right\}\phi_N(\mathbf{R}) = E_{tot}\phi_N(\mathbf{R})$$

i.e., the nuclei move in a potential created by the electrons.

What are we neglecting in BO approximation?

Following Jensen: *We have extra terms in the nuclei Hamiltonian due to other electronic levels and center of mass motion*

Small parameter

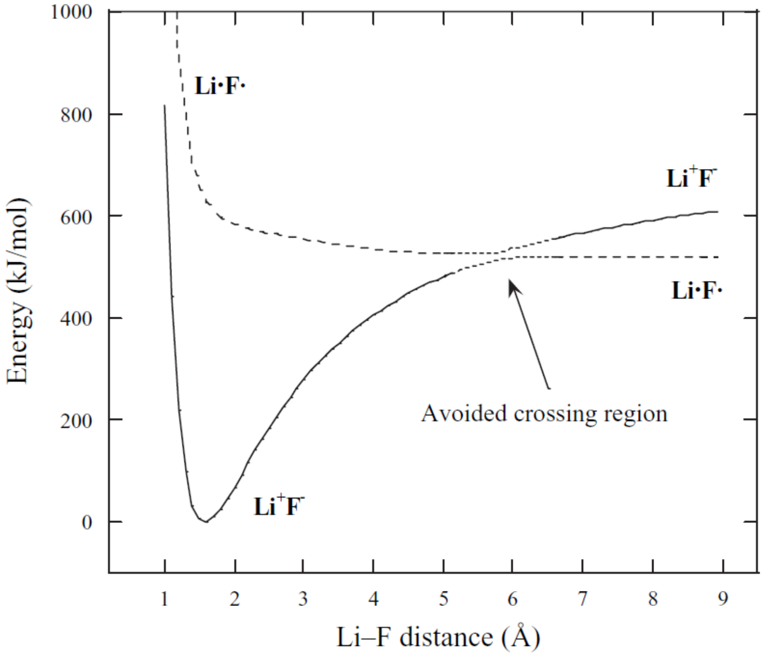
$$m/M_A \sim 1/10000$$

$$\Psi_{\text{tot}}(\mathbf{R},\mathbf{r}) = \sum_{i=1}^{\infty} \Psi_{\text{n}i}(\mathbf{R})\Psi_i(\mathbf{R},\mathbf{r})$$

i and j run over the electronic levels

$$\nabla_{\text{n}}^2\Psi_{\text{n}j} + E_j\Psi_{\text{n}j} + \sum_{i=1}^{\infty}\begin{Bmatrix} 2\langle\Psi_j|\overset{\boxed{1}}{\nabla_{\text{n}}}|\Psi_i\rangle(\nabla_{\text{n}}\Psi_{\text{n}i}) + \langle\Psi_j|\overset{\boxed{2}}{\nabla_{\text{n}}^2}|\Psi_i\rangle\Psi_{\text{n}i} + \\ \langle\Psi_j|\mathbf{H}_{\text{mp}}|\Psi_i\rangle\Psi_{\text{n}i} \quad \boxed{3} \end{Bmatrix} = E_{\text{tot}}\Psi_{\text{n}j}$$

1) First order non-adiabatic terms: VERY IMPORTANT!!! (make Born-Oppenheimer approximation invalid in the vicinity of any electronic level crossing)



2) The diagonal correction (small compared to E_i, accounted in adiabatic approximation, neglected in BO approximation)

3) Mass-polarization (cannot separate the center of mass motion from the internal motion of particles)

$$\mathbf{H}_{\text{mp}} = -\frac{1}{2M_{\text{tot}}}\left(\sum_{i}^{N_{\text{elec}}}\nabla_i\right)^2$$

The electronic structure problem: overview

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_{iA}\frac{Z_A}{r_{iA}} + \sum_{i>j}\frac{1}{r_{ij}}\right]\psi_e(\mathbf{r};\mathbf{R}) = E_e\psi_e(\mathbf{r};\mathbf{R})$$

- A system of fermions interacting via Coulomb potential in electrostatic field of nuclei

- **Problem 1** – one-electron problem: use finite basis set (atomic-like orbitals STO/GTO or plane waves)

- **Problem 2** – many-body problem: use mean field (HF, DFT, TDDFT) and perturbation theories (MP2, CI, CC) in Fock space (basis of Slater determinants)

Method	*Explicit e-correlations*	*Wave-function*	*Cost (PC)*
Ab initio *(MP2, CI, CAS-CI, CC-EOM)*	*All* *(depends on level of theory)*	*Exact* *(for given basis set)*	*Large* *(≥10 electrons)*
Density Functional *(DFT, TDDFT)*	*Dynamic only*	*Kohn-Sham* *(a single-det. "fit" to e-density)*	*Significant* *(≤1000 atoms)*
Semiempirical *(AM1, PM7, ZINDO)*	*Coulomb, exchange, static*	*Hartree-Fock* *(variationally optim. single-det.)*	*Low* *(≤10 000 atoms)*
Tight-binding *(Huckel, Frenkel, DFTB)*	*No*	*One-electron* *(total e-energy is inaccurate)*	*Approach MM* *(>10 000 atoms)*

Wavefunction approach: a systematic way to seek an exact answer

The wavefunction for our 'exact' Hamiltonian should be more complex than a single Slater determinant

A better wavefunction will give lower ground state energy respecting variational principle:

$$\Psi = a_0 \Phi_{\mathrm{HF}} + \sum_{i=1} a_i \Phi_i$$

Correlation energy: $E_{\mathrm{C}}^{\mathrm{trad}} = E - E^{\mathrm{HF}}$

atom	E^{HF}	E	E_{C}
He	-2.862	-2.904	-0.042
Be	-14.571	-14.667	-0.096
Ne	-128.555	-128.938	-0.383

Example: correlations energies for noble gas atoms (in Hartrees)

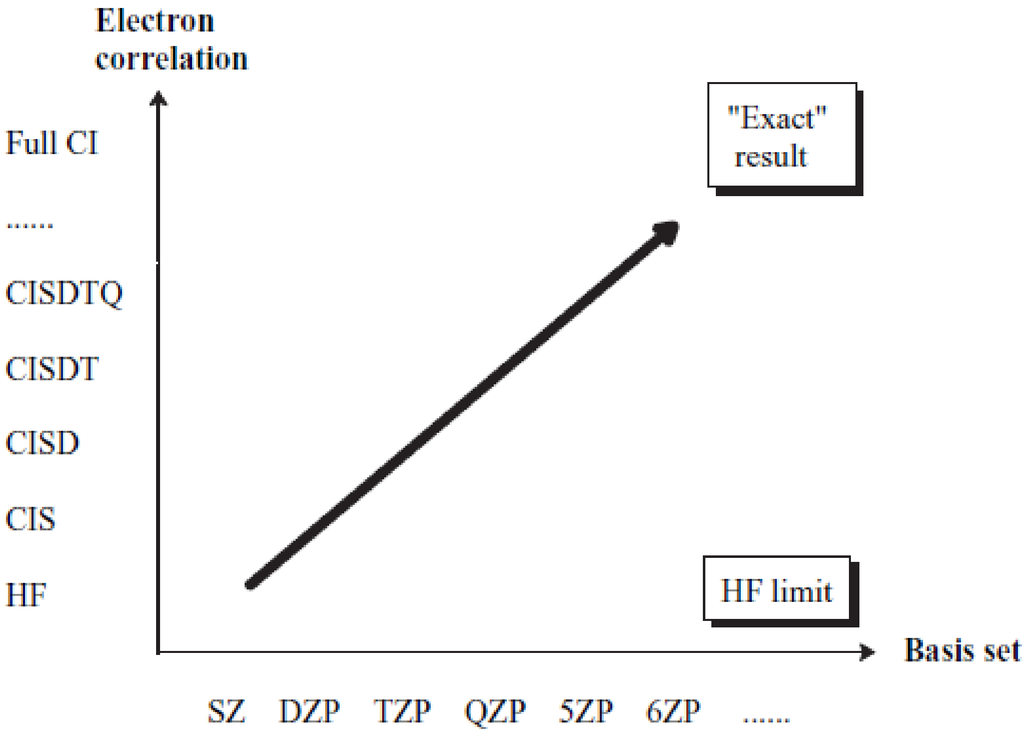


Figure 4.3 (from Jensen)
Convergence to the exact solution

Solving one-electron problem: Atomic orbitals and the LCAO approach

The LCAO concept: construct a guess wave function ϕ as a linear combination of known atomic wave functions φ

$$\phi = \sum_{i=1}^{N} a_i \varphi_i$$

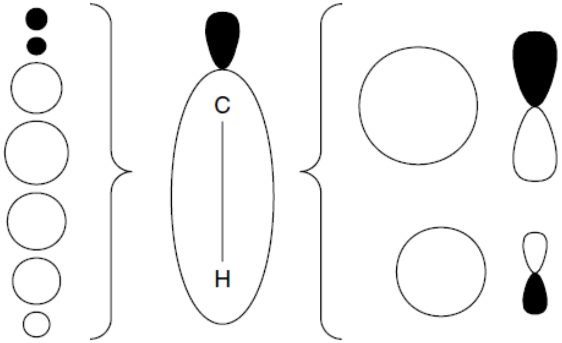


Figure 4.1 from Cramer: Two basis sets for representing a C–H σ bonding orbital

Variational principle leads to a secular equation

$$\frac{\int \Phi H \Phi d\mathbf{r}}{\int \Phi^2 d\mathbf{r}} \geq E_0$$

$$E = \frac{\int \left(\sum_i a_i\varphi_i\right) H \left(\sum_j a_j\varphi_j\right) d\mathbf{r}}{\int \left(\sum_i a_i\varphi_i\right)\left(\sum_j a_j\varphi_j\right) d\mathbf{r}} = \frac{\sum_{ij} a_i a_j H_{ij}}{\sum_{ij} a_i a_j S_{ij}}$$

Resonant and overlap integrals

$$H_{ij} = \int \varphi_i H \varphi_j d\mathbf{r}$$

$$S_{ij} = \int \varphi_i \varphi_j d\mathbf{r}$$

For a minimum $\frac{\partial E}{\partial a_k} = 0$ i.e.,

$$\sum_{i=1}^{N} a_i (H_{ki} - ES_{ki}) = 0$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1N} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2N} - ES_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & \cdots & H_{NN} - ES_{NN} \end{vmatrix} = 0$$

N roots: eigenvalues (E) and eigenvectors (a_i) defining molecular orbitals (MO)

What is our basis set?

$$\{\chi_n(\mathbf{r})\}, \quad n = 1, \ldots, K$$

$$\chi(\mathbf{x}) = \begin{cases} \psi(\mathbf{r})\alpha(\omega) \\ \text{or} \\ \psi(\mathbf{r})\beta(\omega) \end{cases}$$

Basis set = the 'room' for electrons to occupy!

This is a fundamental approximation in ALL electronic structure calculations!

The foundation of every electronic structure code = only one 'type' of the basis set is used in the program

The choice of the basis set type is just a balance between numerical efficiency and physical nature of the electronic wavefunctions to be described!

Common examples: Slater (exponential), Gaussian, polynomial, plane waves, wavelets, cube functions, ….

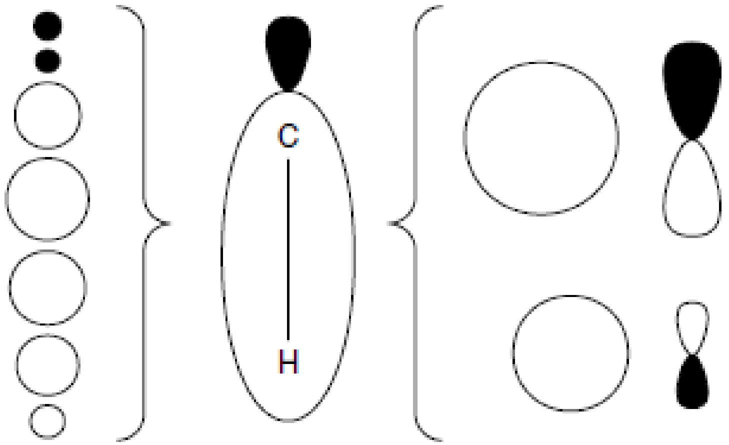


Figure 4.1 (from Cramer) Two different basis sets for representing a C–H σ bonding orbital with the size of the basis functions roughly illustrating their weight in the hybrid MO.

Example 1: Slater-type orbitals (STO)

$$\varphi(r,\theta,\phi;\zeta,n,l,m)=\frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}}r^{n-1}e^{-\zeta r}Y_l^m(\theta,\phi)$$

Atom-centered polar coordinates: ζ is a Slater exponent (Slater rules, 1930) that depend on the atomic number, *n* is the principal quantum number for the valence orbital, and the spherical harmonic functions $Y_m^l\ (\vartheta,\varphi)$, depending on the angular momentum quantum numbers *l* and *m*, (from solution of the Schrödinger equation for the hydrogen atom)

Advantages: chemically intuitive, physically transparent, ‘tails’ of the wavefunctions are important

Disadvantages: numerically difficult (2e integrals need to be evaluated numerically)

Where used: small molecules semiempirical approaches (few 2e integrals), density functional theory (kernels without exact exchange)

Package: ADF (Amsterdam Density Functional)

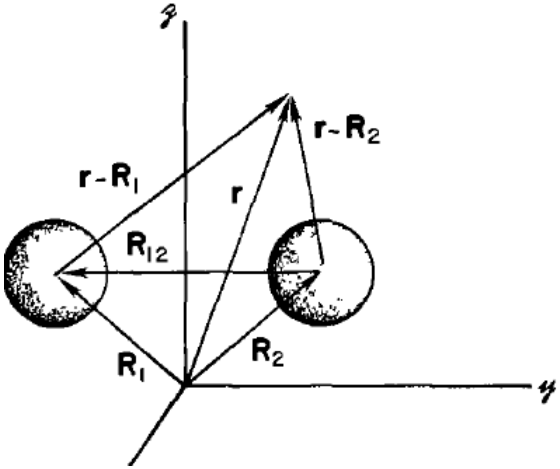
Example: H_2 molecule (from Szabo)

$$\phi(\mathbf{r}-\mathbf{R})=(2\alpha/\pi)^{3/4}e^{-\alpha|\mathbf{r}-\mathbf{R}|^2}$$ (1s orbital for H)

$$S_{12}=\int d\mathbf{r}\ \phi_1^*(\mathbf{r})\phi_2(\mathbf{r})$$ (overlap)

$$\psi_1=[2(1+S_{12})]^{-1/2}(\phi_1+\phi_2)$$
$$\psi_2=[2(1-S_{12})]^{-1/2}(\phi_1-\phi_2)$$

(bonding and antibonding MOs, the HF solutions for H_2)



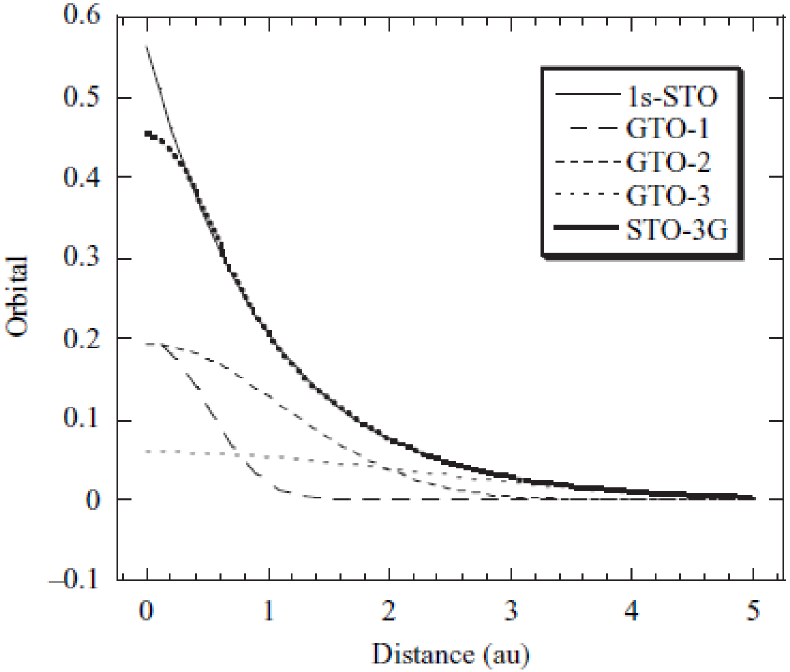
Example 2: Gaussian-type orbitals (GTO)

$$\phi(x,y,z;\alpha,i,j,k) = \left(\frac{2\alpha}{\pi}\right)^{3/4}\left[\frac{(8\alpha)^{i+j+k}\,i!\,j!\,k!}{(2i)!(2j)!(2k)!}\right]^{1/2} x^i y^j z^k e^{-\alpha(x^2+y^2+z^2)}$$

Idea: *Fit Slater-type atomic orbitals with a superposition of Gaussian orbitals*

$$\varphi(x,y,z;\{\alpha\},i,j,k) = \sum_{a=1}^{M} c_a \phi(x,y,z;\alpha_a,i,j,k)$$

Generally 3 GTO fit well 1 STO:



Advantages: chemically intuitive, physically transparent for finite size molecules, numerically easy (2e integrals are evaluated analytically)

Disadvantages: ‘tails’ of the wavefunctions are ‘too short’, no ‘cusp’ of the wavefunction near nuclei, issues with over-completeness and orthogonalization in extended sets

Where used: majority of electronic structure modeling (both wavefunction and DFT methods) in the finite size molecules

Package: Gaussian, Turbomole, Q-Chem, GAMESS, Firefly, etc.

Evaluation of integrals is analytic:

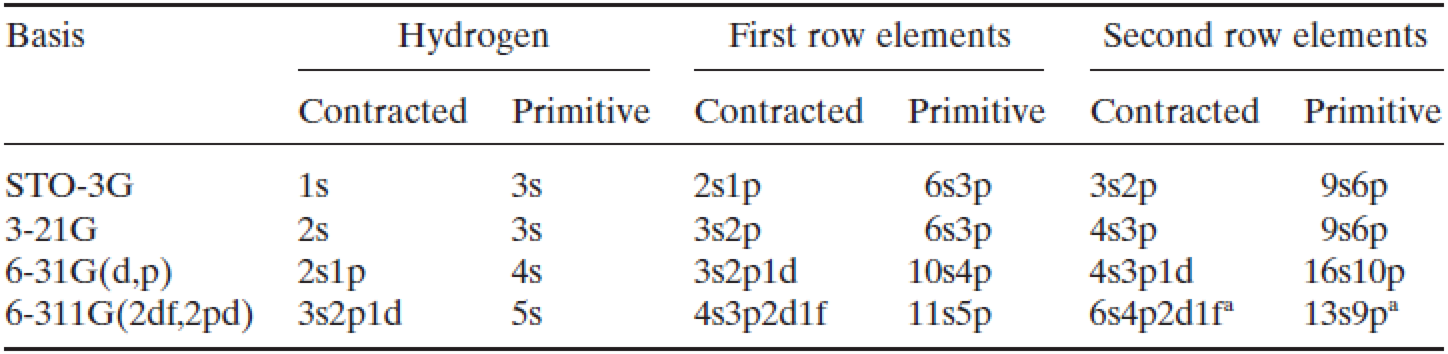
$$\phi_s^{GF}(\alpha,\mathbf{r}-\mathbf{R_A})\;\phi_s^{GF}(\beta,\mathbf{r}-\mathbf{R_B}) = K_{AB}\phi_s^{GF}(p,\mathbf{r}-\mathbf{R_P})$$

$$\langle m_A k_B | n_C l_D\rangle = K_{AB}K_{CD}\int d\mathbf{r}_1 d\mathbf{r}_2\,\phi_s^{GF}(p,\mathbf{r}_1-\mathbf{R_P})\,r_{12}^{-1}\,\phi_s^{GF}(q,\mathbf{r}_2-\mathbf{R_Q})$$

GTO extravaganza

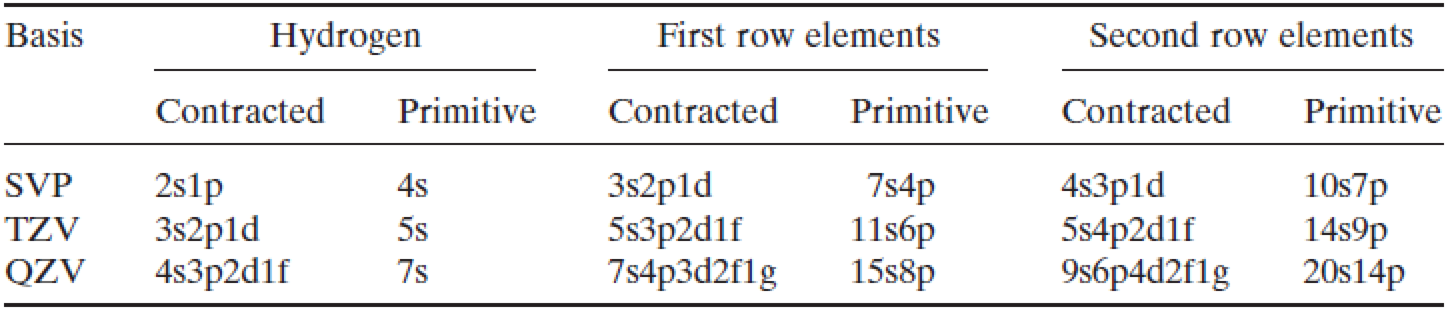
- *Contracted basis set: GTO basis function is a FIXED superposition of primitive GFs*
- *Minimum basis set: the smallest BS able only to host electrons on an atom*
- *Double zeta (DZ) basis set: doubling of all basis functions (tighter and diffuse exp)*
- *Split valence basis set: doubling of all basis functions only on valence orbitals*
- *Triple Zeta (TZ), triple split valence, Quadruple Zeta (QZ), Pentuple Zeta (PZ)….*
- *Adding polarization (e.g. TZP) and diffuse functions*

Table 5.1 (from Jensen): The Pople-style basis sets



Basis	Hydrogen		First row elements		Second row elements	
	Contracted	Primitive	Contracted	Primitive	Contracted	Primitive
STO-3G	1s	3s	2s1p	6s3p	3s2p	9s6p
3-21G	2s	3s	3s2p	6s3p	4s3p	9s6p
6-31G(d,p)	2s1p	4s	3s2p1d	10s4p	4s3p1d	16s10p
6-311G(2df,2pd)	3s2p1d	5s	4s3p2d1f	11s5p	6s4p2d1f[a]	13s9p[a]

Table 5.2 (from Jensen): The Ahlrichs type basis sets



Basis	Hydrogen		First row elements		Second row elements	
	Contracted	Primitive	Contracted	Primitive	Contracted	Primitive
SVP	2s1p	4s	3s2p1d	7s4p	4s3p1d	10s7p
TZV	3s2p1d	5s	5s3p2d1f	11s6p	5s4p2d1f	14s9p
QZV	4s3p2d1f	7s	7s4p3d2f1g	15s8p	9s6p4d2f1g	20s14p

Just 6-31+G*

C: $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$

Lots of choices!

STO-3G 3-21G
4-31G 6-31G
6-31G* 6-31+G*
6-311+G** D95V
LANL2DZ SDD
SVP TZV

Inner shell (each 6 GF)	$1s$
Valence shell (2 sets, each 3 GF)	$2s$ $2p_x$ $2p_y$ $2p_z$ $2's$ $2'p_x$ $2'p_y$ $2'p_z$
Diffuse functions: + (next shell, each 3 GF)	$3s$ $3p_x$ $3p_y$ $3p_z$
Polarized functions: * (next shell, each 3 GF)	$3d_{xx}$ $3d_{yy}$ $3d_{zz}$ $3d_{xy}$ $3d_{xz}$ $3d_{yz}$

Total 19 basis functions

Example 3: Plane waves

Idea: Use cos/sin forms of wavefunction following solution (waves) of the free-electron motion problem:

$$\phi(x) = A\cos(kx) + B\sin(kx)$$

$$E = \tfrac{1}{2}k^2$$

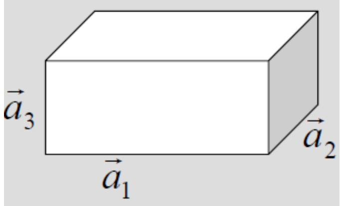
Plane wave expansion

$$u_n(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{i_1=1}^{N_1} \sum_{i_2=1}^{N_2} \sum_{i_3=1}^{N_3} \tilde{u}_n\left(\vec{G}_{i_1 i_2 i_3}\right) e^{i\vec{G}_{i_1 i_2 i_3}\cdot\vec{r}}$$

PBC constrain $e^{i\vec{G}\cdot(\vec{r}+\vec{R})} = e^{i\vec{G}\cdot\vec{r}}$

Constrains on the wavevectors:

$$\vec{G}_{i_1 i_2 i_3} = \left(i_1 - \frac{N_1}{2}\right)\vec{b}_1 + \left(i_2 - \frac{N_2}{2}\right)\vec{b}_2 + \left(i_3 - \frac{N_3}{2}\right)\vec{b}_3$$



Volume of the cell

$$\Omega = [\vec{a}_1, \vec{a}_2, \vec{a}_3] = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$$

$$\chi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}$$

Advantages: Orthogonal basis set, numerically ‘easy’ integrals, friendly to the *k*-space and Periodic Boundary Conditions (PBC), no Pulay forces for fixed cell

Disadvantages: Necessity of PBC, the basis set size/computational complexity grows significantly with the size of the periodic cell, necessity of using pseudopotentials.

Where used: majority of electronic structure modeling (mostly DFT methods) in periodic systems

Package: VASP, NWChem, ABINIT, etc.

Reciprocals vectors

$$\vec{b}_1 = 2\pi\frac{\vec{a}_2 \times \vec{a}_3}{\Omega}$$

$$\vec{b}_2 = 2\pi\frac{\vec{a}_3 \times \vec{a}_1}{\Omega}$$

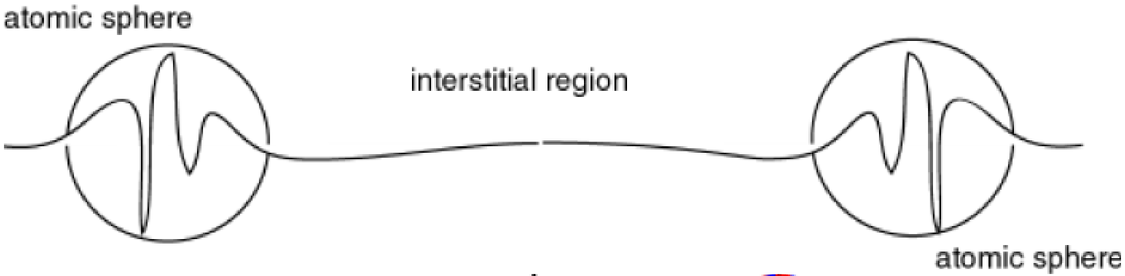
$$\vec{b}_3 = 2\pi\frac{\vec{a}_1 \times \vec{a}_2}{\Omega}$$

Energy cut-off

$$\frac{1}{2}\left|\vec{G}\right|^2 < E_{cut}$$

Pseudopotentials:

Problem: near nuclei, electronic wavefunctions/densities have highly oscillating behavior. Core electrons do not participate in chemical bonds.

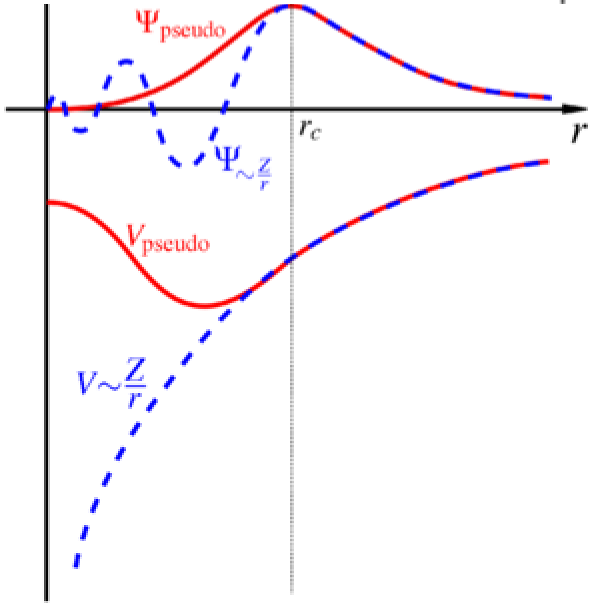


The pseudopotential replaces the complicated effects of the motion of the core (i.e. non-valence) electrons of an atom and its nucleus with an effective potential, which implicitly take into account relativistic effects for core electrons. Coulombic potential -> effective potential term in the Schrödinger equation for the rest of electrons. By construction of this pseudopotential, the valence wavefunction generated is also guaranteed to be orthogonal to all the core states.

$$\left(H + V^R\right)\left|\tilde{\psi}^v\right\rangle = E_v\left|\tilde{\psi}^v\right\rangle$$

$$V^R\left|\tilde{\psi}^v\right\rangle = \sum_c \left(E_v - E_c\right)\left|c\right\rangle\left\langle c\middle|\tilde{\psi}^v\right\rangle$$

The pseudopotentials are particularly necessary for plane wave calculations but also useful for Gaussian basis sets for heavy atoms (e.g. LANL2DZ ~ 6-31G for valence electrons)



From Wikipedia: Comparison of a wavefunction in the Coulomb potential of the nucleus (blue) to the one in the pseudopotential (red). The real and the pseudo wavefunction and potentials match above a certain cutoff radius **r_c**

Individual studies:

- ***Reading.***

Required: *Cramer (Ch. 4)*
Additional: *Jensen (Ch. 1.8.1, 3.1-3.4)*
Szabo (Ch. 2.1, 2.2)

Solution in detail for Hydrogen atom
http://web.mst.edu/~sparlin/phys107/lecture/chap06.pdf
http://www.nat.vu.nl/~wimu/EDUC/MNW-lect-2.pdf

Advanced reading:
A fresh look to Born-Oppenheimer approximation from Hardy Gross – new definition of potential energy surfaces

[1] A. Abedi, N. T. Maitra and E. K. U. Gross, Phys. Rev. Lett., 105, 123002, (2010).
[2] A. Abedi, N. T. Maitra and E. K. U. Gross, J. Chem. Phys., 137, 22A530, (2012).