

CHEM6085: Density Functional Theory

Lecture 2

Hamiltonian operators for molecules

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The (time-independent) Schrödinger equation is an **eigenvalue equation**

$$\hat{A} f_n(x) = a_n f_n(x)$$

operator for property A eigenfunction eigenvalue

$$\hat{H} \Psi_n(x) = E_n \Psi_n(x)$$

Energy operator (Hamiltonian) wavefunction Energy eigenvalue

Constructing operators in Quantum Mechanics

Quantum mechanical operators **are the same** as their corresponding classical mechanical quantities

	Classical quantity	Quantum operator
position	x	x

Potential energy (e.g. energy of attraction of an electron by an atomic nucleus)	$V(x)$	$V(x)$
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With one exception!

The momentum operator is completely different:

$$mv_x \longrightarrow -i\hbar \frac{d}{dx}$$

Building Hamiltonians

The Hamiltonian operator (=total energy operator) is a sum of two operators: the kinetic energy operator and the potential energy operator

$$\hat{H} = \hat{T} + \hat{V}$$

Kinetic energy requires taking into account the momentum operator

$$T = \frac{1}{2}mv_x^2 = \frac{(mv_x)^2}{2m}$$

The potential energy operator is straightforward

$$\hat{V} = V(x)$$

$$\hat{T} = \frac{1}{2m} \left(-i\hbar \frac{d}{dx} \right) \left(-i\hbar \frac{d}{dx} \right) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

The Hamiltonian becomes:
$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

Expectation values of operators

- Experimental measurements of physical properties are average values
- Quantum mechanics postulates that we can calculate the result of any such measurement by “averaging” the appropriate operator and the wavefunction as follows:

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} \Psi^*(x) \hat{x} \Psi(x) dx}{\int_{-\infty}^{\infty} \Psi^*(x) \Psi(x) dx}$$

The above example provides the expectation value (average value) of the position along the x-axis.

Force between two charges: Coulomb's Law

Like charges repel
Unlike charges attract

$$F = \frac{kq_1q_2}{r^2} = \frac{q_1q_2}{4\pi\epsilon_0 r^2} \quad \text{Coulomb's Law}$$

$\left| \leftarrow \text{---} \mathbf{r} \text{---} \rightarrow \right|$

Energy of two charges

$$E_{q_1q_2} = \frac{1}{4\pi\epsilon_0} \frac{q_1q_2}{|\mathbf{r}|}$$

$$|\mathbf{r}| = \sqrt{x^2 + y^2 + z^2}$$

$$|\mathbf{r}| = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2} = |\mathbf{r}_2 - \mathbf{r}_1|$$

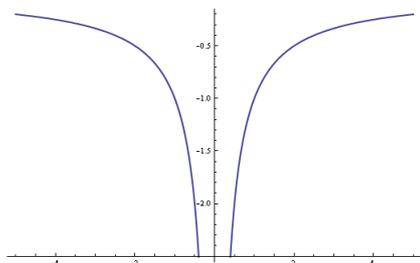
Coulomb potential energy (or operator)

$$E_{q_1 q_2} = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{|\mathbf{r}|} = q_1 \boxed{\frac{q_2}{4\pi\epsilon_0 |\mathbf{r}|}}$$

Examples:

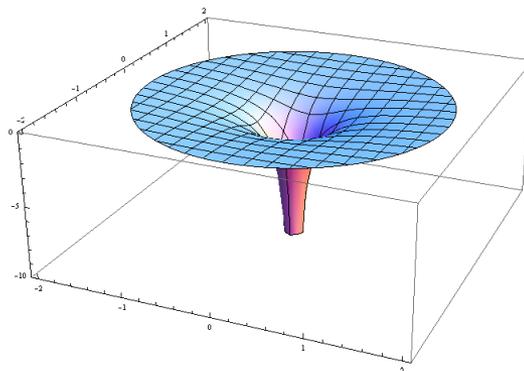
In one dimension

$$-\frac{1}{|\mathbf{r}|} = -\frac{1}{|x|}$$



In 2 dimensions

$$-\frac{1}{|\mathbf{r}|} = -\frac{1}{\sqrt{x^2 + y^2}}$$

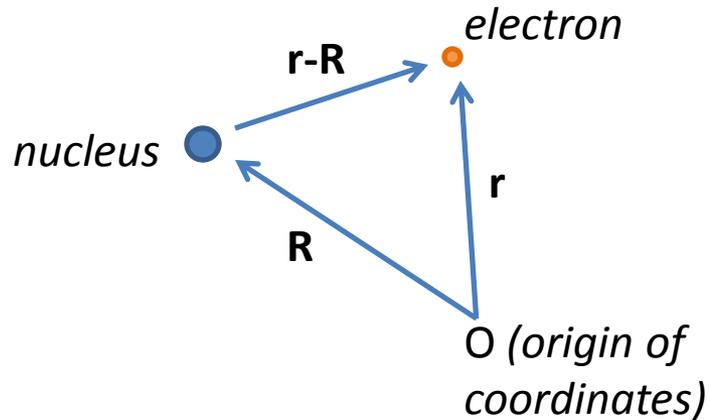


In 3 dimensions

$$-\frac{1}{|\mathbf{r}|} = -\frac{1}{\sqrt{x^2 + y^2 + z^2}}$$

- Difficult to visualise (would require a 4-dimensional plot!)
- We live in a 3-dimensional world so this is the potential we use

Hamiltonian for hydrogen atom



$$\hat{H} = \underbrace{-\frac{\hbar^2}{2M} \left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right)}_{\text{nuclear kinetic energy}} - \underbrace{\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)}_{\text{electronic kinetic energy}} - \underbrace{\frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r} - \mathbf{R}|}}_{\text{electron-nucleus attraction}}$$

$$\hat{H} = -\frac{\hbar^2}{2M} \nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 - \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r} - \mathbf{R}|}$$

Atomic units

We will use **Atomic Units** as they simplify quantum chemistry expressions.

E.g.:

In SI units:
$$\hat{H} = -\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 - \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{r} - \mathbf{R}|}$$

In atomic units:
$$\hat{H} = -\frac{1}{2M}\nabla_{\mathbf{R}}^2 - \frac{1}{2}\nabla_{\mathbf{r}}^2 - \frac{1}{|\mathbf{r} - \mathbf{R}|}$$

Quantity	Atomic Unit	Value in SI
Energy	$\hbar^2/m_e a_0$ (Hartree)	4.36×10^{-18} J
Charge	e	1.60×10^{-19} C
Length	a_0	5.29×10^{-11} m
Mass	m_e	9.11×10^{-31} kg

Born-Oppenheimer approximation

For a molecule, the wavefunction is a function of the coordinates of all the electrons and all the nuclei:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_{\text{electrons}}}, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_{\text{atoms}}})$$

- The Born-Oppenheimer approximation is based on the fact that nuclei have much larger masses than the electrons
- To a good approximation, one can solve the Schrödinger equation only for the electrons and assume the nuclei are frozen
- We will use this approximation from now on
- As a result, our wavefunctions will be functions only of electronic coordinates:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_{\text{electrons}}})$$

Average energy

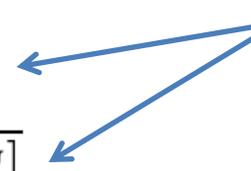
The energy operator is the Hamiltonian. For a molecular system, under the B.O. approximation, this is

$$\langle E \rangle = \langle H \rangle = \frac{\int \int \cdots \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_{\text{electrons}}}) \hat{H} \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_{\text{electrons}}}) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_{N_{\text{electrons}}}}{\int \int \cdots \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_{\text{electrons}}}) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_{\text{electrons}}}) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_{N_{\text{electrons}}}}$$

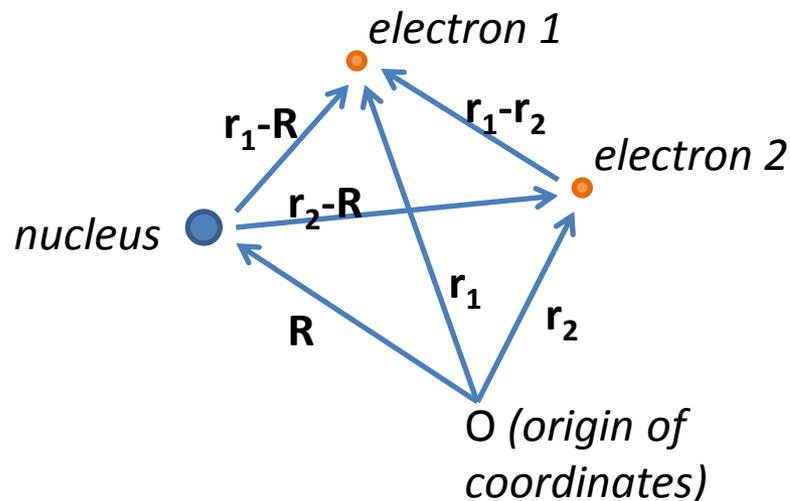
We can write this also as

$$\langle E \rangle = \frac{F_E[\Psi]}{F_{\text{Norm}}[\Psi]}$$

Functionals of Ψ



Hamiltonian for helium atom



B.O.

$$\hat{H} = -\cancel{\frac{1}{2M}}\nabla_{\mathbf{R}}^2 - \frac{1}{2}\nabla_{\mathbf{r}_1}^2 - \frac{1}{2}\nabla_{\mathbf{r}_2}^2 - \frac{2}{|\mathbf{r}_1 - \mathbf{R}|} - \frac{2}{|\mathbf{r}_2 - \mathbf{R}|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

kinetic
energy of
nucleus

kinetic
energy of
electron 1

kinetic
energy of
electron 2

attraction of
electron 1 by
nucleus

attraction of
electron 2 by
nucleus

repulsion
between
electrons 1
and 2

Sums Σ

- Extremely useful shorthand notation
- Allows to condense summations with many terms (5, 10, 100, many millions, infinite!) into one compact expression

Single sum example:

$$q_1 \mathbf{r}_1 + q_2 \mathbf{r}_2 + q_3 \mathbf{r}_3 = \sum_{n=1}^3 q_n \mathbf{r}_n$$

Double sum example:

$$\begin{aligned} & (x_1 - y_1) + (x_1 - y_2) + (x_1 - y_3) + (x_2 - y_1) + (x_2 - y_2) + (x_2 - y_3) \\ &= \sum_{i=1}^3 (x_1 - y_i) + \sum_{j=1}^3 (x_2 - y_j) \\ &= \sum_{k=1}^2 \sum_{i=1}^3 (x_k - y_i) \end{aligned}$$

Hamiltonian operator for water molecule

Water contains 10 electrons and 3 nuclei. We will use the symbols "O" for the oxygen (atomic number $Z_O=8$) nucleus, "H1" and "H2" (atomic numbers $Z_{H1}=1$ and $Z_{H2}=1$) for the hydrogen nuclei.

$$\hat{H}_{H_2O} = -\frac{\cancel{1}^{\text{B.O.}}}{\cancel{2M_O}} \nabla_{\mathbf{R}_O}^2 - \frac{\cancel{1}^{\text{B.O.}}}{\cancel{2M_{H1}}} \nabla_{\mathbf{R}_{H1}}^2 - \frac{\cancel{1}^{\text{B.O.}}}{\cancel{2M_{H2}}} \nabla_{\mathbf{R}_{H2}}^2 - \sum_{i=1}^{10} \frac{1}{2} \nabla_{\mathbf{r}_i}^2$$

Kinetic energy of O
 Kinetic energy of H1
 Kinetic energy of H2
 Kinetic energy of electron i

$$- \sum_{i=1}^{10} \frac{8}{|\mathbf{r}_i - \mathbf{R}_O|} - \sum_{i=1}^{10} \frac{1}{|\mathbf{r}_i - \mathbf{R}_{H1}|} - \sum_{i=1}^{10} \frac{1}{|\mathbf{r}_i - \mathbf{R}_{H2}|}$$

Electron attraction to O
 Electron attraction to H1
 Electron attraction to H2

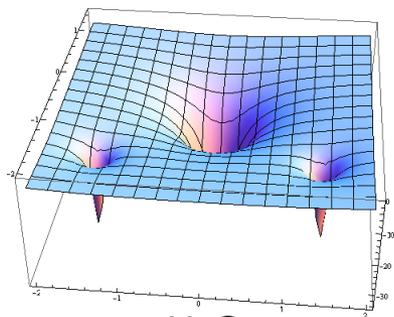
$$+ \sum_{i=1}^{10} \sum_{j=i+1}^{10} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I=1}^3 \sum_{J=I+1}^3 \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

Electron-electron repulsion
 nucleus-nucleus repulsion

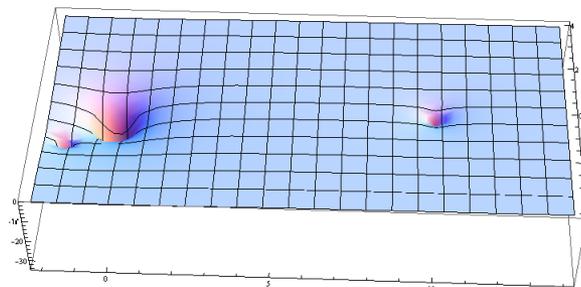
E.g. Assume
 $Z_1=Z_O$
 $Z_2=Z_{H1}$
 $Z_3=Z_{H2}$

- Quite a complicated expression! Hamiltonians for molecules become intractable
- Fortunately, we do not need to write all this for every molecule we study. We can develop general, much more compact expressions that apply to any molecule, irrespective of its size

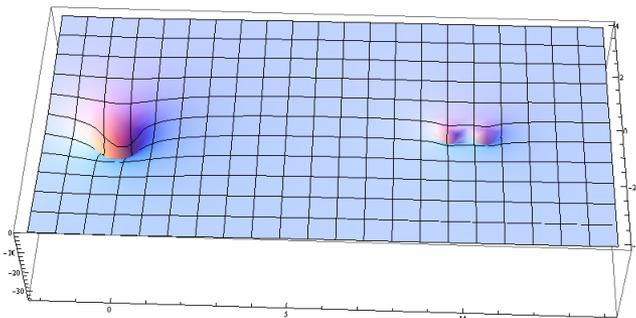
Example: Nuclear attraction potential for one O and two H



H₂O



OH + H



O + H₂

- How does the Hamiltonian operator differ between these examples?
- Can you suggest how you may model the reaction OH+H → H₂O

Homework

- 1) Use summation symbols to generalise the example of the water molecule from the lectures to an expression for the electronic Hamiltonian operator of **any** molecule, with any number of nuclei and electrons.
- 2) Write down an expression for the expectation value of each of the terms of the above Hamiltonian (i.e. Kinetic energy, electron-electron repulsion energy, etc.)
- 3) Assume that charged particles such as electrons and nuclei, instead of having electrostatic interactions that obey Coulomb's Law (and included in the Hamiltonian in terms of Coulomb potential energy expressions) have interactions that obey Hooke's Law, which gives the potential energy of two particles connected by a spring as $\frac{1}{2}k(x-x_0)^2$, where x_0 is the equilibrium distance (spring is fully relaxed) and x is its current distance. Write down the electronic Hamiltonian operator for the He atom in this case.

