CHEM3023: Spins, Atoms and Molecules

Lecture 2

Bra-ket notation and molecular Hamiltonians

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Learning outcomes

- Be able to manipulate quantum chemistry expressions using bra-ket notation
- Be able to construct Hamiltonian operators for molecules

Dirac's "bra-ket" shorthand notation

- Paul Dirac introduced a shorthand notation for quantum chemical integrals that greatly simplifies written expressions without any loss in information
- This notation has been widely adopted and we will also use it throughout this course

$$\int \Psi^*(\mathbf{x})\,\hat{C}\,\Phi(\mathbf{x})\,d\mathbf{x} \quad \text{becomes} \quad \langle\Psi|\hat{C}|\Phi\rangle$$

A "bra"

$$\langle\Psi| \equiv \int d\mathbf{x}\,\Psi^*(\mathbf{x})$$

A "ket"

$$|\Phi\rangle \equiv \Phi(\mathbf{x})$$

Write the Schrödinger equation in bra-ket notation

Bra-ket notation practice

Starting from the Schrödinger equation, write down an expression for the energy

Integral form

$$\hat{H}\psi(\mathbf{x}) = E\psi(\mathbf{x})$$

$$\psi^*(\mathbf{x})\hat{H}\psi(\mathbf{x}) = \psi^*(\mathbf{x})E\psi(\mathbf{x})$$

$$\int \psi^*(\mathbf{x})\hat{H}\psi(\mathbf{x})d\mathbf{x} = \int \psi^*(\mathbf{x})E\psi(\mathbf{x})d\mathbf{x}$$

$$\int \psi^*(\mathbf{x})\hat{H}\psi(\mathbf{x})d\mathbf{x} = E\int \psi^*(\mathbf{x})\psi(\mathbf{x})d\mathbf{x}$$

$$E = \frac{\int \psi^*(\mathbf{x})\hat{H}\psi(\mathbf{x})d\mathbf{x}}{\int \psi^*(\mathbf{x})\psi(\mathbf{x})d\mathbf{x}}$$

Bra-ket form

$$\hat{H}|\psi\rangle = E|\psi\rangle$$

$$\langle\psi|\hat{H}|\psi\rangle = \langle\psi|E|\psi\rangle$$

$$\langle\psi|\hat{H}|\psi\rangle = E\langle\psi|\psi\rangle$$

$$E = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}$$

Bra-ket notation practice

Write down the following in bra-ket notation

$$\int f(\mathbf{x})\, g^*(\mathbf{x}) d\mathbf{x} \qquad \int f(\mathbf{x})\, g(\mathbf{x}) d\mathbf{x} \qquad \int f^*(\mathbf{x})\, g(\mathbf{x}) d\mathbf{x} \qquad \int f^*(\mathbf{x})\, g^*(\mathbf{x}) d\mathbf{x}$$

$$\psi(\mathbf{x}) \int \psi^*(\mathbf{x}') f(\mathbf{x}') d\mathbf{x}' \qquad \int f^*(\mathbf{x})[a\, g(\mathbf{x}) + b\, h(\mathbf{x})] d\mathbf{x}$$

$$\int f^*(\mathbf{x}) \hat{H} \hat{H} g(\mathbf{x}) d\mathbf{x} \qquad \int f^*(\mathbf{x})(\hat{H}_1 + \hat{H}_2) g(\mathbf{x}) d\mathbf{x}$$

$$\int \psi^*(x)\, \frac{d}{dx} \phi(x) dx$$

Bra-ket notation practice (continued)

- Assume that for the operator *A* the following is true: $\langle \phi | \hat{A} | \psi \rangle = \langle \psi | \hat{A} | \phi \rangle^*$
- f_i are the eigenfunctions of A, with eigenvalue equation: $\hat{A} f_i = a_i f_i$

$$\langle f_i | \hat{A} | f_i \rangle = \langle f_i | \hat{A} | f_i \rangle^*$$

$$\langle f_i | a_i | f_i \rangle = \langle f_i | a_i | f_i \rangle^*$$

$$a_i \langle f_i | f_i \rangle = a_i^* \langle f_i | f_i \rangle^*$$

$$(a_i - a_i^*) \langle f_i | f_i \rangle = 0$$

$$a_i = a_i^*$$

Therefore the eigenvalues of *A* are real numbers.

Re-derive this result using integral notation

Hermitian operators

An operator which satisfies the following relation

$$\langle f|\hat{C}|g\rangle = \langle g|\hat{C}|f\rangle^*$$

is called Hermitian

- We showed that Hermitian operators have real eigenvalues
- All experimentally observable quantities are real numbers
- As a result quantum mechanical operators that represent observable properties (e.g. energy, dipole moment, etc.) must be Hermitian

Constructing operators in Quantum Mechanics

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

	Classical quantity		Quantum operator
position	x	$\longrightarrow$	x
Potential (e.g. energy of attraction of an electron by an atomic nucleus)	$V(x)$	$\longrightarrow$	$V(x)$

With one exception!

The momentum operator is completely different:

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

Building Hamiltonians

The Hamiltonian operator is the total energy operator and is a sum of

(1) the kinetic energy operator, and
(2) the potential energy operator

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

The kinetic energy is made up from the momentum operator

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

The potential energy operator is straightforward

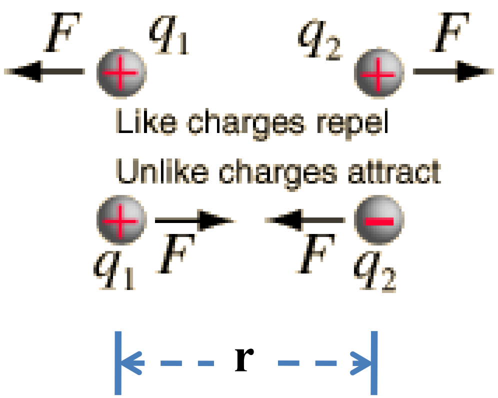
$$\hat{V} = V(x)$$

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

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

Force between two charges: Coulomb’s Law

Electrons and nuclei are charged particles



$$F = \frac{kq_1q_2}{r^2} = \frac{q_1q_2}{4\pi\varepsilon_0 r^2}$$

Coulomb's Law

Energy of two charges

$$E_{q_1q_2} = \frac{1}{4\pi\varepsilon_0}\frac{q_1q_2}{|\mathbf{r}|}$$

Distance between charge q_1 at point $\mathbf{r}_1$ and charge q_2 at point $\mathbf{r}_2$

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

Coulomb potential (or operator)

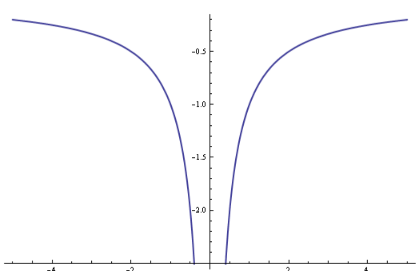
$$E_{q_1 q_2} = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{|\mathbf{r}|} = q_1 \boxed{\frac{q_2}{4\pi\varepsilon_0|\mathbf{r}|}} = q_1 \boxed{V_{q_2}}$$

Coulomb potential of charge q_2

Examples:

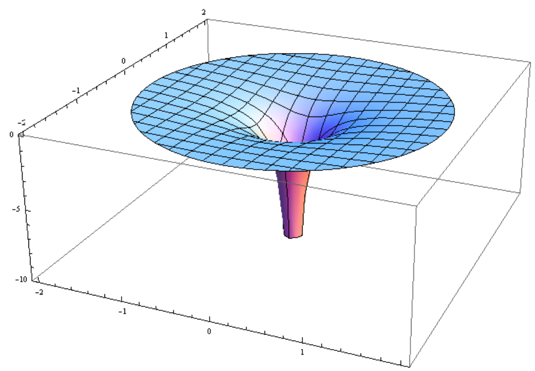
In one dimension

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



In 2 dimensions

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

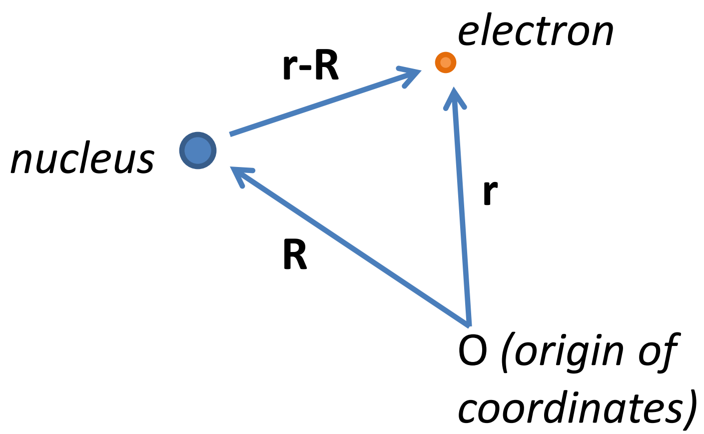


In 3 dimensions

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

- 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



nuclear kinetic energy — electronic kinetic energy — electron-nucleus attraction

$$\hat{H} = -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}\right) - \frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\mathbf{r}-\mathbf{R}|}$$

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} - \frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\mathbf{r}-\mathbf{R}|}$$

Atomic units

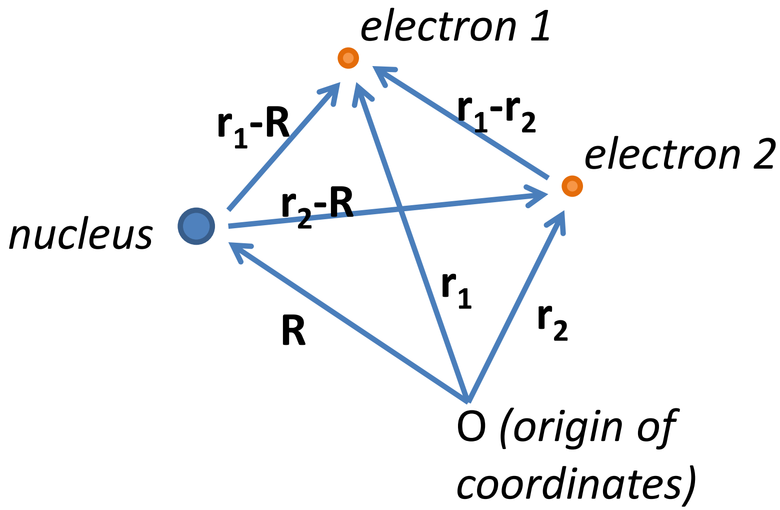
They simplify quantum chemistry expressions. E.g.:

In SI units: $$\hat{H} = -\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} - \frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\mathbf{r}-\mathbf{R}|}$$

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

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

Hamiltonian for Helium atom



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

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 $\sum$

- 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:

$$(x_1 - y_1) + (x_1 - y_2) + (x_1 - y_3) + (x_2 - y_1) + (x_2 - y_2) + (x_2 - y_3)$$

$$= \sum_{i=1}^{3}(x_1 - y_i) + \sum_{j=1}^{3}(x_2 - y_j)$$

$$= \sum_{k=1}^{2}\sum_{i=1}^{3}(x_k - y_i)$$

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.

$$\hat{H}_{\mathrm{H_2O}} = -\frac{1}{2M_{\mathrm{O}}}\nabla^2_{\mathbf{R}_{\mathrm{O}}} - \frac{1}{2M_{\mathrm{H1}}}\nabla^2_{\mathbf{R}_{\mathrm{H1}}} - \frac{1}{2M_{\mathrm{H2}}}\nabla^2_{\mathbf{R}_{\mathrm{H2}}} - \sum_{i=1}^{10}\frac{1}{2}\nabla^2_{\mathbf{r}_i}$$

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

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

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 expressions that are much more compact and apply to any molecule, irrespective of size

Summary / Reading assignment

- Bra-ket notation (Atkins, page 16)
- Rules for writing operators in quantum mechanics, constructing molecular Hamiltonian operators (Cramer, page 106)
- Atomic units (Cramer, page 15)