# Quantum Chemistry

Lecture 8

Braket Notation
Hermitian Operators
Normalization

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# Braket Notation

# Braket Notation

The formulation of mathematical formulation of quantum mechanics involves numerous integrals. We have already shown that the average energy (or expectation value) for the n*th* eigenstate of a system can be expressed as

$$\langle E_n \rangle = \frac{\int \Psi_n^* H \Psi_n d\tau}{\int \Psi_n^* \Psi_n d\tau}$$

Integrals of this type are so common and expressions can become so complex that Dirac developed an alternative formulation. In this formulation we can write an integral as a braket

$$\int \Psi_n^* \Psi_n d\tau = \langle n|n \rangle$$

The significance of the braket is further that it can be viewed as the inner (or dot) product of two vectors. Thus, it is shorthand notation for a vector space. In the case above, where |n> is a normalized wave function, the inner product is clearly

$$\langle n|n\rangle = 1$$

However, in the general case we may consider two complex vectors A and B, which have an inner product

$$\langle A|B\rangle = A_x^* B_x + A_y^* B_y + A_z^* B_z$$

In this example we have considered a Cartesian space. In this space we could express the vector B in one of two ways:

$$|B> = B_x|e_x> + B_y|e_y> + B_z|e_z> \qquad |B> = \begin{pmatrix} B_x \\ B_y \\ B_z \end{pmatrix}$$

Thus, the inner product can also be expressed as:

$$\langle A|B\rangle = \begin{pmatrix} A_x^* & A_y^* & A_z^* \end{pmatrix} \begin{pmatrix} B_x \\ B_y \\ B_z \end{pmatrix}$$

This is scalar multiplication since the result is a scalar.

A linear operator can operate on a ket. For example, the momentum operator is

$$\hat{p}_x|k> = -i\hbar \frac{\partial}{\partial x}|k>$$

Keeping in mind the ket also can represent a wave function, we may consider that this wave function in this instance is:

$$|k> = e^{ikx}$$

In that case our operator equation would give the result.

$$-i\hbar \frac{\partial}{\partial x}|k> \;\; \hbar k|k>$$

# Using Operators in the Braket

The bra or left hand part always signifies that the complex conjugate is the be used. Thus, we do not need to write the star. The wave function is thus written in a more complex notation as

$$\Psi_n = |n>$$

In an operator equation the braket has the form

$$\int \Psi_n^* H \Psi_n d\tau = \langle n|H|n\rangle$$

An operator O can act either on the (from the left) or on the bra (from the right).

$$(< n|O)|m> =< n|(O|m>)$$

When the operator operates from the left it has the complex conjugate form.

We often simply write the quantum numbers of the given wave function in the bra or ket as a shorthand notation. In this way we can represent the wave function of the hydrogen atom as $|\mathrm{n}\ell\mathrm{m}>$ so that all of the quantum numbers are shown.

The shorthand notation of the braket has double meaning. It can be used to represent integrals such as the energy given above. However, we can also think if the braket as dot product, i.e. a projection of one wave function onto another.

When the quantum numbers in the bra equal those in the ket We have a condition for normalization. When the quantum Numbers are not equal then the braket is zero if the wave Functions are part of an orthonormal set. Since solutions of The Schrodinger equation are part of such a set this fact Can used to prove important theorems of quantum mechanics.

# Hermitian Operators

A Hermitian operator is defined by the condition that the operator should be equal to its self-adjoint. For the operator O we express this as

$$\hat{O}^{\dagger} = \hat{O}$$

The self-adjoint is the transpose complex conjugate of a matrix. For a single operator this implies that the operator equation is equal to its complex conjugate,

$$\hat{O}^{*}\psi^{*} = \hat{O}\psi$$

# Hermitian Operators must have real eigenvalues

The reason that this mathematical statement is important is that it is the key aspect of the proof that the eigenvalue of an operator equation will be real. To see this, we let the eigenvalues of P be called $p_i$ and $p_j$. Then,

$$\langle \psi_i | \widehat{P} \psi_j \rangle = p_j \langle \psi_i | \psi_j \rangle \text{ and } \langle \widehat{P} \psi_i | \psi_j \rangle = p_i^* \langle \psi_i | \psi_j \rangle$$

However, since $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ these will vanish unless i = j.

$$p_j = p_j^*$$

which tells us that the eigenvalues are real and that they are identical.

# General Normalization

In the general case where a wave function is not normalized we can determined the normalization constant.
The normalization constant N is defined by

$$\Psi = \mathrm{N}\psi$$

. To determine N, we can write,

$$\langle\Psi|\Psi\rangle = \mathrm{N}^2\langle\psi|\psi\rangle = 1$$

Therefore,

$$\mathrm{N} = \frac{1}{\sqrt{\langle\psi|\psi\rangle}}$$

The normalized wave function is

$$\Psi = \frac{1}{\sqrt{\langle\psi|\psi\rangle}}\psi$$

# Angular Momentum Operators

The definitions of the angular momentum operators in spherical polar coordinates are:

$$\hat{L}_x = -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

The total angular momentum is:

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

which can be expressed in terms of the angular derivatives,

$$\hat{L}^2 = -\hbar^2\left(\frac{1}{\sin\phi}\frac{\partial}{\partial\theta}\sin\phi\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\phi}\frac{\partial^2}{\partial\phi^2}\right)$$

# Raising and Lowering Operators

We can define a raising and lowering operator for angular momentum using the definition:

$$\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y$$

This is also known as the ladder operator, and it has the form,

$$\hat{L}_{\pm} = -i\hbar e^{\pm i\phi}\left(\pm i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\phi}\right)$$

We can prove the valuation of the angular momentum commutators

$$\left[\hat{L}_z, \hat{L}_{\pm}\right] = \pm\hbar\hat{L}_{\pm} \qquad \left[\hat{L}_+, \hat{L}_-\right] = 2\hbar\hat{L}_z$$

based on an evaluation of eigenvalues.

# Evaluation of the operators

We can use the nomenclature

$$Y^{\ell}_{m}(\theta, \phi) = |\ell, m>$$

From the known properties of the angular momentum operator in obtained in the solution of the angular equation we have:

$$\hat{L}_z|\ell, m> = \hbar m|\ell, m>$$

$$\hat{L}^2|\ell, m> = \hbar^2 \ell(\ell + 1)|\ell, m>$$

We can use the commutator to evaluate the ladder operator,

$$\hat{L}_{\pm}|\ell, m>$$

We want to evaluate the ladder operator using,

$$\hat{L}_z\left(\hat{L}_{\pm}|\ell, m>\right)$$

Using the definition of the commutator we have

$$\hat{L}_z\hat{L}_\pm - \hat{L}_\pm\hat{L}_z = \pm\hbar\hat{L}_\pm$$

$$\hat{L}_z\hat{L}_\pm|\ell, m> = \hat{L}_\pm\hat{L}_z|\ell, m> \pm\hbar\hat{L}_\pm|\ell, m>$$

$$\hat{L}_z\hat{L}_\pm|\ell, m> = \hat{L}_\pm\hbar m|\ell, m> \pm\hbar\hat{L}_\pm|\ell, m>$$

$$\hat{L}_z\hat{L}_\pm|\ell, m> = \hbar(m \pm 1)\hat{L}_\pm|\ell, m>$$

Thus, we see that the raising/lowering operator is an eigenstate of $L_z$ with eigenvalue of

$$\hbar(m \pm 1)$$

This shows that

$$\hat{L}_\pm|\ell, m> = c^\pm|\ell, m \pm 1>$$

We can show that the eigenvalue for the ladder operators is,

$$c^\pm = \hbar\sqrt{\ell(\ell + 1) - m(m \pm 1)}$$

# Identities based on angular momentum operators

From the definition of the total angular moment, we can replace the x and y terms using the definition of the ladder operator,

$$\hat{L}_x^2 + \hat{L}_y^2 = \left(\hat{L}_x + i\hat{L}_y\right)\left(\hat{L}_x - i\hat{L}_y\right) = \frac{1}{2}\hat{L}_+\hat{L}_-$$

From the commutator we have

$$\hat{L}_+\hat{L}_- = \hat{L}_-\hat{L}_+ + 2\hbar\hat{L}_z$$

Therefore,

$$\hat{L}^2 = \frac{1}{2}\hat{L}_-\hat{L}_+ + \hbar\hat{L}_z + \hat{L}_z^2$$

There are $2\ell + 1$ values of m, which range from -$\ell$ to $\ell$. If we operate on the highest eigenfunction with the ladder operator, We obtain 0, i.e.

$$\hat{\mathrm{L}}_+|\ell,\ell> = 0$$

Likewise,

$$\hat{\mathrm{L}}_-|\ell,-\ell> = 0$$

Thus, if we choose $|\ell,\ell>$ as our test function we have,

$$\hat{\mathrm{L}}^2\left|\ell,\ell> = \frac{1}{2}\hat{\mathrm{L}}_-\hat{\mathrm{L}}_+\right|\ell,\ell> + \hbar\hat{\mathrm{L}}_z\,|\ell,\ell> + \hat{\mathrm{L}}_z^2\,|\ell,\ell>$$

This gives,

$$\hat{\mathrm{L}}^2|\ell,\ell> = 0 + \hbar(\hbar\ell)|\ell,\ell> + (\hbar\ell)^2|\ell,\ell>$$

Thus,

$$\hat{\mathrm{L}}^2|\ell,\ell> = \hbar^2\ell(\ell+1)|\ell,\ell>$$