

QUANTUM MECHANICS, BRAS AND KETS

The following summarizes the main relations and definitions from quantum mechanics relevant to PH575.

State of a physical system:

The state of a physical system is represented by a “state vector” or “ket” and it is denoted by a symbol such as $|\psi\rangle$.

Like an ordinary vector, the ket can be expressed as a linear combination of “basis kets” $|\phi_i\rangle$ with coefficients c_i :

$$|\psi\rangle = \sum_i c_i |\phi_i\rangle.$$

The basis ket $|\phi_i\rangle$ is often abbreviated simply by $|i\rangle$.

The corresponding “bra” is $\langle\psi| = \sum_i c_i^* \langle i|$ where c_i^* is the complex conjugate of c_i .

The ket is an abstract quantity that represents a quantum state. Often, we wish to be more specific an explicit representation that gives us information about (for example) spatial (position) distribution of electron density. To do this, we “project” the ket onto the bras that are the eigenstates of position. The resulting function is called the wave function (in the position representation). An explicit example of a set of basis wave functions is the set of hydrogen ground state orbitals used to develop the states of the diatomic molecule, linear chain, etc.:

$$\varphi_i(r) = \left(\frac{1}{4\pi}\right)^{1/2} \frac{2}{\sqrt{a_0^3}} e^{-r/a_0}$$

where a_0 is the Bohr radius and r_i is the radial distance of the electron from the i^{th} nucleus.

(We will rarely use the explicit forms of these basis functions. Rather we make use of their mathematical properties such as orthogonality and normalization – see below.)

Projections – scalar products:

The coefficients in the linear combination are the projections of $|\psi\rangle$ on the basis states $|i\rangle$, i.e. $c_i = \langle i|\psi\rangle$ where the object $\langle i|\psi\rangle$ is a scalar product analogous to the “dot” product of ordinary vectors. The scalar product of two state vectors (or the projection of one on the other) is a sum of products of their respective projections on the basis (again just like ordinary vectors: $\vec{a} \cdot \vec{b} = a_x b_x + a_y b_y + a_z b_z$). Thus,

$$\langle\psi|\xi\rangle = \sum_i \langle\psi|i\rangle \langle i|\xi\rangle.$$

If we were using explicit functions of spatial coordinates to represent the states $|\psi\rangle$ and $|\xi\rangle$, we would evaluate the projection with an integral

$$\langle\psi|\xi\rangle = \int_{\text{all space}} \psi^*(\vec{r}) \xi(\vec{r}) dV.$$

The quantity $\langle \psi | \xi \rangle$ is often called the "overlap integral". It represents "how much" of one function is "contained" in another. The overlap integral of orthogonal functions (see below) is either zero or one.

The orthonormal property usually assumed for the basis states can be expressed in terms of their scalar products:

$$\langle j | i \rangle = 1 \text{ if } i = j; \langle j | i \rangle = 0 \text{ if } i \neq j.$$

This same statement is often written in terms of the Kronecker delta:

$$\langle j | i \rangle = \delta_{ij}$$

State vectors $|\psi\rangle$ are usually normalized: $\langle \psi | \psi \rangle = 1$. This leads to the result that

$$\sum_i c_i^* c_i = \sum_i |c_i|^2 = 1$$

The quantity $|c_i|^2$ is the probability that in a measurement, an electron will be found in the particular basis state $|i\rangle$. The normalization condition simply expresses the fact that the electron must be found in *some* basis state, thus the sum of all probabilities equals 1.

Operators

In quantum mechanics, observable physical quantities are represented by operators.

There are two cases to consider:

Case I: An operator L "operates" on a state vector $|\psi\rangle$ and yields the same state vector simply multiplied by a constant:

$$L|\psi\rangle = C_L|\psi\rangle.$$

In this case, $|\psi\rangle$ is an "eigenvector" of the operator L and the constant C_L is an "eigenvalue." The most important example of this is given by the Schrödinger equation

$$H|\psi\rangle = E|\psi\rangle$$

where the Hamiltonian (energy operator) is, in Cartesian spatial coordinates,

$$H = \text{kinetic} + \text{potential energy} = \frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x, y, z) = \frac{-\hbar^2}{2m} \nabla^2 + V(x, y, z)$$

A state vector that satisfies the Schrödinger equation is an energy eigenfunction or eigenvector with eigenvalue equal to the energy of the state E . An important part of the determination of the electronic structure of solids is to determine the energy eigenvalues for particular assemblies of atoms.

Case II: The state vector $|\psi\rangle$ is NOT an eigenvector of the operator L . In this case the operation of L on $|\psi\rangle$ produces a *different* state vector or linear combination of state vectors, denoted here by $|\xi\rangle$:

$$L|\psi\rangle = \text{constant} \times |\xi\rangle.$$

The matrix elements of an operator L are expressed in terms of a particular basis set $|i\rangle$. They are scalar products of a basis bra $\langle j|$ and the ket produced by the action of L on $|i\rangle$, i.e. $\langle j|L|i\rangle = L_{ji}$.

When $i = j$, the “diagonal” matrix element $\langle i|L|i\rangle = L_{ii}$ is the “expectation value” of the physical quantity represented by L in the particular basis state $|i\rangle$. If, in addition, $|i\rangle$ is an eigenvector of L , then L_{ii} is just the eigenvalue C_L . For example, if L is the energy operator H and our basis states are the atomic ground states, then H_{ii} is the energy of an electron in the ground state of atom i .

Specific examples of the above with reference to the hydrogen atom atomic orbitals.

State of a physical system:

Suppose the state of an electron in a H-atom is an unequal superposition of the $1s$ and $2p_z$ states. We denote this “state vector” or “ket” by $|\psi\rangle$.

$|\psi\rangle$ can be expressed as a linear combination of “basis kets” $|\phi_i\rangle$, which in this case are the eigenstates of the H-atom Hamiltonian. In this case the basis kets $|\phi_i\rangle$ are $|1s\rangle$ and $|2p_z\rangle$. The coefficients c_i in this case are not equal, and for illustration are set in a 1:2 ratio. Proper normalization requires that the squares of the coefficients sum to 1:

$$|\psi\rangle = \sum_i c_i |\phi_i\rangle = \frac{1}{\sqrt{5}} |1s\rangle + \frac{2}{\sqrt{5}} |2p_z\rangle.$$

The basis kets $|\phi_i\rangle$ could also be labeled by the quantum numbers, n, l, m_l , of the state: $|100\rangle$ and $|210\rangle$.

The corresponding “bra” is $\langle\psi| = \sum_i c_i^* \langle i|$ where c_i^* is the complex conjugate of c_i .

For an explicit representation that gives information about spatial (position) distribution of electron density, we “project” the ket onto the bras that are the eigenstates of position. The resulting functions are called the wave functions (in the position representation). Here, the basis wave functions are the hydrogen orbitals:

$$\varphi_{1s}(r, \theta, \phi) = \frac{2}{\sqrt{a_0^3}} e^{-r/a_0} \cdot \left(\frac{1}{4\pi}\right)^{1/2}, \quad \varphi_{2p_z}(r, \theta, \phi) = \frac{1}{2\sqrt{\pi}} \left(\frac{r}{2a_0}\right)^{3/2} e^{-r/2a_0} \cos\theta$$

where a_0 is the Bohr radius and r is the radial distance of the electron from the nucleus.

Projections – scalar products:

Project the state $|\psi\rangle$ onto the $1s$ basis state: The notation is: $\langle 1s|\psi\rangle$

Project the state $|\psi\rangle$ onto the $2p_z$ basis state: The notation is: $\langle 2p_z|\psi\rangle$

Projections are really integrals. The notation $\langle | \rangle$ means integrate over all space, in

this case in 3 spatial dimensions: $\int_{x=-\infty}^{\infty} \int_{y=-\infty}^{\infty} \int_{z=-\infty}^{\infty} \dots dx dy dz$ or $\int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{r=0}^{\infty} \dots r^2 \sin\theta dr d\theta d\phi$.

The notation $|\psi\rangle$ means insert the function $\psi(r,\theta,\phi)$ into the integral and the notation

$\langle 1s|$ means insert the complex conjugate function $\phi_{1s}^*(r,\theta,\phi)$ into the integral. Thus:

$$\langle 1s|\psi\rangle = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{r=0}^{\infty} \phi_{1s}^*(r,\theta,\phi)\psi(r,\theta,\phi)r^2 \sin\theta dr d\theta d\phi.$$

Because we can look up the position representation of basis wave functions, we can plug in and evaluate. But because the basis functions of the Hamiltonian are orthogonal to one another, the integration is not necessary (but you should check that it actually does evaluate to 1 or zero)!

$$\langle 1s|\psi\rangle = \langle 1s|\left(\frac{1}{\sqrt{5}}|1s\rangle + \frac{2}{\sqrt{5}}|2p_z\rangle\right) = \frac{1}{\sqrt{5}}\underbrace{\langle 1s|1s\rangle}_1 + \frac{2}{\sqrt{5}}\underbrace{\langle 1s|2p_z\rangle}_0 = \frac{1}{\sqrt{5}}$$

$$\langle 2p_z|\psi\rangle = \langle 1s|\left(\frac{1}{\sqrt{5}}|1s\rangle + \frac{2}{\sqrt{5}}|2p_z\rangle\right) = \frac{1}{\sqrt{5}}\underbrace{\langle 2p_z|1s\rangle}_0 + \frac{2}{\sqrt{5}}\underbrace{\langle 2p_z|2p_z\rangle}_1 = \frac{2}{\sqrt{5}}$$

The scalar product of two state vectors (or the projection of one on the other) is a sum of products of their respective projections on the basis (again just like ordinary vectors:

$\vec{a} \cdot \vec{b} = a_x b_x + a_y b_y + a_z b_z$). Suppose another state of the H-atom is represented by

$$|\xi\rangle = \frac{1}{\sqrt{2}}|1s\rangle + \frac{1}{\sqrt{2}}|3p_x\rangle. \text{ Then the projection of } |\xi\rangle \text{ onto } |\psi\rangle \text{ is}$$

$$\begin{aligned} \langle \psi|\xi\rangle &= \left(\frac{1}{\sqrt{5}}\langle 1s| + \frac{2}{\sqrt{5}}\langle 2p_z|\right)\left(\frac{1}{\sqrt{2}}|1s\rangle + \frac{1}{\sqrt{2}}|3p_x\rangle\right) \\ &= \frac{1}{\sqrt{10}}\underbrace{\langle 1s|1s\rangle}_1 + \frac{1}{\sqrt{10}}\underbrace{\langle 1s|3p_x\rangle}_0 + \frac{2}{\sqrt{10}}\underbrace{\langle 2p_z|1s\rangle}_0 + \frac{2}{\sqrt{10}}\underbrace{\langle 2p_z|3p_x\rangle}_0 = \frac{1}{\sqrt{10}} \\ \langle \psi|\xi\rangle &= \sum_i \langle \psi|i\rangle\langle i|\xi\rangle. \end{aligned}$$

Or we could evaluate the projection with the integral

$$\langle \psi|\xi\rangle = \int_{\text{all space}} \psi^*(\vec{r})\xi(\vec{r})dV.$$

The quantity $\langle \psi|\xi\rangle$ is often called the "overlap integral". It represents "how much" of one function is "contained" in another. The overlap integral of orthogonal functions (see below) is either zero or one.

Operators

Case I: The Hamiltonian operator $H = \frac{-\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$ “operates” on a state vector and yields the same state vector simply multiplied by a constant. Examples are the states $|1s\rangle, |2p_z\rangle, |3p_x\rangle$.

$$H|1s\rangle = \frac{-e^2}{2(4\pi\epsilon_0)a_0} |1s\rangle; \quad H|2p_z\rangle = \frac{-e^2}{2(2)^2(4\pi\epsilon_0)a_0} |2p_z\rangle; \quad H|3p_x\rangle = \frac{-e^2}{2(3)^2(4\pi\epsilon_0)a_0} |3p_x\rangle$$

In this case $|1s\rangle, |2p_z\rangle, |3p_x\rangle$ are eigenstates of the operator H , which is why we chose them as the basis states. The eigenvalues are the energies of the respective orbitals.

Case II: The Hamiltonian operator $H = \frac{-\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$ “operates” on a state vector and yields a different state vector (multiplied by some constant). Examples are $|\psi\rangle$ and $|\xi\rangle$, which are NOT eigenvalues of H . For example, $H|\psi\rangle = \frac{-e^2}{\sqrt{5}2a_0} |\gamma\rangle$ where the ket $|\gamma\rangle$ is found below:

$$\begin{aligned} H|\psi\rangle &= H \left(\underbrace{\frac{1}{\sqrt{5}}|1s\rangle + \frac{2}{\sqrt{5}}|2p_z\rangle}_{|\psi\rangle} \right) \\ &= \frac{1}{\sqrt{5}} \frac{-e^2}{2(4\pi\epsilon_0)a_0} |1s\rangle + \frac{2}{\sqrt{5}} \frac{-e^2}{2(4\pi\epsilon_0)a_0(2)^2} |2p_z\rangle = \frac{-e^2}{\sqrt{5}2(4\pi\epsilon_0)a_0} \left(\underbrace{|1s\rangle + \frac{1}{4}|2p_z\rangle}_{|\gamma\rangle} \right) \end{aligned}$$

The matrix elements of the Hamiltonian H are expressed in terms of a particular basis set $|i\rangle$. They are scalar products of a basis bra $\langle j|$ and the ket produced by the action of H on $|i\rangle$, i.e. $\langle j|H|i\rangle = H_{ji}$. If the basis vectors are eigenfunctions, the matrix is diagonal. For example:

$$\begin{aligned} H_{1s,1s} &= \langle 1s|H|1s\rangle = E_{1s} \langle 1s|1s\rangle = E_{1s} \\ H_{1s,2s} &= \langle 1s|H|2s\rangle = E_{2s} \langle 1s|2s\rangle = E_{1s} \cdot 0 = 0 \end{aligned}$$

The matrix is (in part ... it is actually infinite in dimension):

$$H \begin{matrix} |1s\rangle & |2s\rangle & |2p_x\rangle & |2p_y\rangle & |2p_z\rangle & |3s\rangle \end{matrix}$$

$$\begin{matrix} |1s\rangle \\ |2s\rangle \\ |2p_x\rangle \\ |2p_y\rangle \\ |2p_z\rangle \\ |3s\rangle \end{matrix} \begin{pmatrix} E_1 & 0 & 0 & 0 & 0 & 0 \\ 0 & E_2 & 0 & 0 & 0 & 0 \\ 0 & 0 & E_2 & 0 & 0 & 0 \\ 0 & 0 & 0 & E_2 & 0 & 0 \\ 0 & 0 & 0 & 0 & E_2 & 0 \\ 0 & 0 & 0 & 0 & 0 & E_3 \end{pmatrix}$$

The “diagonal” matrix element $\langle i|L|i\rangle = L_{ii}$ is called the “expectation value” of the physical quantity represented by L in the particular basis state $|i\rangle$.

Using the same basis states to express the L_z operator, we find the matrix is NOT diagonal because the p_x and p_y states are not eigenfunctions of the L_z operator. The matrix is (in part ... it is actually infinite in dimension):

$$L_z \begin{matrix} |1s\rangle & |2s\rangle & |2p_x\rangle & |2p_y\rangle & |2p_z\rangle & |3s\rangle \end{matrix}$$

$$\begin{matrix} |1s\rangle \\ |2s\rangle \\ |2p_x\rangle \\ |2p_y\rangle \\ |2p_z\rangle \\ |3s\rangle \end{matrix} \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \neq 0 & 0 & 0 \\ 0 & 0 & \neq 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

There are many places to look up the H atom wave functions and find more examples of bras, kets and operators. A good resource is the PH425 text book, "Quantum Mechanics", David H. McIntyre (Pearson, 2nd printing). Your text book for PH575, Sutton, has some in Eqs 1.21 and 1.22.