

## Quantum Mechanical Operators and Commutation C

### I. Bra-Ket Notation

It is conventional to represent integrals that occur in quantum mechanics in a notation that is independent of the number of coordinates involved. This is done because the fundamental structure of quantum chemistry applies to all atoms and molecules, regardless of how many electronic and atom-center coordinates arise. The most commonly used notation, which is referred to as 'Dirac' or 'bra-ket' notation, can be summarized as follows:

A. The wavefunction itself is represented as a so-called 'ket'  $|\psi\rangle$ .

B. The complex conjugate  $\psi^*$  of  $\psi$  is represented as a 'bra'  $\langle\psi|$ ; the complex conjugation is implied by writing  $\langle\psi|$ .

C. The integral, over all of the  $N$  coordinates  $(q_1 \dots q_N)$  on which  $\psi$  depends, of the product of  $\psi^*$  and  $\psi$  is represented as a so-called 'bra-ket' or bracket:

$$\int \psi^* \psi dq_1 \dots dq_N = \langle\psi|\psi\rangle.$$

By convention, the two vertical lines that touch when  $\langle\psi|$  is placed against  $|\psi\rangle$  are merged into a single line in this notation.

D. Integrals involving one function  $\psi^*$  and either another function  $\psi$  or the result of an operator  $A$  acting on a function (e.g.,  $A\psi$  or  $A^2\psi$ ) are denoted as follows:

$$* \int dq_1 \dots dq_N = \langle \quad | \quad \rangle$$

$$* \int A \, dq_1 \dots dq_N = \langle \quad | A \quad \rangle = \langle \quad | A | \quad \rangle$$

$$* \int A \, dq_1 \dots dq_N = \langle \quad | A \quad \rangle = \langle \quad | A | \quad \rangle$$

$$(A)^* \int dq_1 \dots dq_N = \langle A \quad | \quad \rangle.$$

It is merely convention that an 'extra' vertical line (e.g., that appearing in  $\langle \quad | A \quad \rangle$ ) is inserted when an operator acting on the ket function appears in the integral.

## II. Hermitian Operators

In quantum mechanics, physically measurable quantities are represented by hermitian operators. Such operators  $\{R\}$  have matrix representations, in any basis spanning the space of functions on which the  $\{R\}$  act, that are hermitian:

$$\langle k | R | l \rangle = \langle l | R | k \rangle^* = \langle R | k | l \rangle.$$

The equality of the first and third terms expresses the so-called 'turn-over rule'; hermitian operators can act on the function to their right or, equivalently, on the function to their left.

Operators that do not obey the above identity are not hermitian. For such operators, it is useful to introduce the so-called adjoint operator as follows. If for the operator  $R$ , another operator  $R^+$  can be found that obeys

$$\langle k | R | l \rangle = \langle R^+ | k | l \rangle = \langle l | R^+ | k \rangle^*,$$

for all  $\{ | k \rangle \}$  within the class of functions on which  $R$  and  $R^+$  operate, then  $R^+$  is defined to be the adjoint of  $R$ . With this definition, it should be clear that hermitian operators are self-adjoint (i.e., they obey  $R^+ = R$ ).

The hermiticity property guarantees that the eigenvalues  $\{ \lambda_m \}$  of such operators are real numbers (i.e., not complex) and that the corresponding eigenfunctions  $\{ f_m \}$ , or their representations  $\{ V_{mk} \}$  within the  $\{ | k \rangle \}$  basis

$$f_m = \sum_k V_{mk} | k \rangle,$$

corresponding to different eigenvalues are orthonormal and that the eigenfunctions belonging to degenerate eigenvalues can be made orthonormal.

To prove these claims, start with  $R | k \rangle = \lambda_k | k \rangle$ . Multiplying on the left by the complex conjugate of  $\langle k |$  and integrating gives  $\langle k | R | k \rangle = \lambda_k \langle k | k \rangle$ . Taking the

complex conjugate of this equation and using the Hermiticity property  $\langle k | R | l \rangle = \langle l | R | k \rangle^*$  (applied with  $k=l$ ) gives  $k^* = k$ .

The orthogonality proof begins with  $R | k \rangle = k | k \rangle$ , and  $R | l \rangle = l | l \rangle$ . Multiplying the first of these on the left by  $\langle l |$  and the second by  $\langle k |$  gives  $\langle l | R | k \rangle = k \langle l | k \rangle$  and  $\langle k | R | l \rangle = l \langle k | l \rangle$ . The complex conjugate of the second reads  $\langle k | R | l \rangle^* = l^* \langle k | l \rangle^*$ ; using the Hermiticity property this reduces to  $\langle l | R | k \rangle = l^* \langle l | k \rangle$ . If  $k \neq l$ , this result can be consistent with  $\langle l | R | k \rangle = k \langle l | k \rangle$  only if  $\langle l | k \rangle$  vanishes.

### III. Meaning of the Eigenvalues and Eigenfunctions

In quantum mechanics, the eigenvalues of an operator represent the only numerical values that can be observed if the physical property corresponding to that operator is measured. Operators for which the eigenvalue spectrum (i.e., the list of eigenvalues) is discrete thus possess discrete spectra when probed experimentally.

For a system in a state that is an eigenfunction of  $R$

$$R \psi = r \psi,$$

measurement of the property corresponding to  $R$  will yield the value  $r$ . For example, if an electron is in a  $2p_{-1}$  orbital and  $L^2$  is measured, the value  $L(L+1) \hbar^2 = 2\hbar^2$  (and only this value) will be observed; if  $L_z$  is measured, the value  $-\hbar$  (and only this value) will be observed. If the electron were in a  $2p_x$  orbital and  $L^2$  were measured, the value  $2\hbar^2$  will be found; however, if  $L_z$  is measured, we can not say that only one value will be observed because the  $2p_x$  orbital is not an eigenfunction of  $L_z$  (measurements in such non-eigenfunction situations are discussed below).

In general, if the property  $R$  is measured, any one of the eigenvalues  $\{ r_m \}$  of the operator  $R$  may be observed. In a large number of such measurements (i.e., for an ensemble of systems all in states described by  $\psi$  that may or may not itself be an eigenfunction of  $R$ ), the probability or frequency of observing the particular eigenvalue  $r_m$  is given by  $|C_m|^2$ , where  $C_m$  is the expansion coefficient of  $\psi$  in the eigenfunctions of  $R$ :

$$\psi = \sum_{\mu} C_{\mu} f_{\mu}.$$

In the special case treated earlier in which  $\psi$  is an eigenfunction of  $R$ , all but one of the  $C_m$  vanish; hence the probability of observing various  $r_m$  values is zero except for the one state for which  $C_m$  is non-zero.

For a measurement that results in the observation of the particular value  $r_m$ , a subsequent measurement of  $R$  on systems just found to have eigenvalue  $r_m$  will result, with 100% certainty, in observation of this same value  $r_m$ . The quantum mechanical interpretation of this experimental observation is to say that the act of measuring the property belonging to the operator  $R$  causes the wavefunction to be altered. Once this

measurement of R is made, the wavefunction is no longer  $\psi$ ; it is now  $f_m$  for those species for which the value  $\lambda_m$  is observed.

For example (this example and others included in this Appendix are also treated more briefly in Chapter 1), if the initial  $\psi$  discussed above were a so-called superposition state of the form

$$\psi = a(2p_0 + 2p_{-1} - 2p_1) + b(3p_0 - 3p_{-1}), \text{ then:}$$

A. If  $L^2$  were measured, the value  $2\hbar^2$  would be observed with probability  $3|a|^2 + 2|b|^2 = 1$ , since all of the non-zero  $C_m$  coefficients correspond to p-type orbitals for this  $\psi$ . After said measurement, the wavefunction would still be this same  $\psi$  because this entire  $\psi$  is an eigenfunction of  $L^2$ .

B. If  $L_z$  were measured for this

$$\psi = a(2p_0 + 2p_{-1} - 2p_1) + b(3p_0 - 3p_{-1}),$$

the values  $0\hbar$ ,  $1\hbar$ , and  $-1\hbar$  would be observed (because these are the only functions with non-zero  $C_m$  coefficients for the  $L_z$  operator) with respective probabilities  $|a|^2 + |b|^2$ ,  $|a|^2$ , and  $|a|^2 + |-b|^2$ .

C. After  $L_z$  were measured, if the sub-population for which  $-1\hbar$  had been detected were subjected to measurement of  $L^2$  the value  $2\hbar^2$  would certainly be found because the new wavefunction

$$\psi' = \{-a(2p_{-1}) - b(3p_{-1})\} (|a|^2 + |b|^2)^{-1/2}$$

is still an eigenfunction of  $L^2$  with this eigenvalue.

D. Again after  $L_z$  were measured, if the sub-population for which  $-1\hbar$  had been observed and for which the wavefunction is now

$$\psi' = \{-a(2p_{-1}) - b(3p_{-1})\} (|a|^2 + |b|^2)^{-1/2}$$

were subjected to measurement of the energy (through the Hamiltonian operator), two values would be found. With probability

$|a|^2 (|a|^2 + |b|^2)^{-1}$  the energy of the  $2p_{-1}$  orbital would be observed; with probability  $|b|^2 (|a|^2 + |b|^2)^{-1}$ , the energy of the  $3p_{-1}$  orbital would be observed.

The general observation to make is that, given an initial normalized  $\psi$  function, and a physical measurement (with operator R) to be made, one first must express  $\psi$  as a linear combination of the complete set of eigenfunctions of that R:

$$\psi = \sum_m C_m f_m.$$

The coefficients  $C_m$  tell, through  $|C_m|^2$ , the probabilities (since  $\psi$  is normalized to unity) of observing each of the  $R$  eigenvalues  $\lambda_m$  when the measurement is made. Once the measurement is made, that sub-population of the sample on which the experiment was run that gave the particular eigenvalue, say  $\lambda_p$ , now have a wavefunction that no longer is the above  $\psi$ ; their wavefunction now is  $\psi_p$ .

#### IV. Experiments Do Not Prepare Only Eigenstates

The above remarks should not be interpreted to mean that experiments are limited to preparing only eigenstates. Just as one can 'pluck' a violin string or 'pound' a drum head in any manner, experiments can prepare a system in states that are not pure eigenfunctions (i.e., states that do not contain just one eigenfunction in their expansion). However, no matter how the state is prepared, it can be interpreted, via expansion in the complete set of eigenfunctions of the operator(s) whose properties are to be measured, as a superposition of eigenfunctions. The superposition amplitudes provide the probabilities of observing each eigenfunction when the measurement is made.

For example, after the drum head has been hit, its shape will evolve spatially and in time in a manner that depends on how it was 'prepared' by the initial blow. However, if one carries out an experiment to detect and frequency-analyze the sound that emanates from this drum, thereby measuring differences in the eigen-energies of the system, one finds a set of discrete (quantized) frequencies  $\{\omega_k\}$  and corresponding amplitudes  $\{A_k\}$ . Repeating this experiment after a different 'blow' is used to prepare a different initial state of the drum head, one finds the same frequencies  $\{\omega_k\}$  but different amplitudes  $\{B_k\}$ .

The quantum mechanics interpretation of these observations is that the initial state of the drum head is a superposition of eigenstates:

$$\psi = \sum_n C_n \psi_n.$$

The  $\{C_n\}$  amplitudes are determined by how the drum head is 'prepared' in the blow that strikes it. As time evolves,  $\psi$  progresses according to the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial \psi}{\partial t} = H \psi.$$

The frequencies emitted by this system will depend on the probability  $|C_n|^2$  of the system being in a particular eigenstate  $\psi_n$  and the energy  $E_n$  of each eigenstate.

The frequency spectrum measured for the drum head motion is therefore seen to have variable amplitudes for each observed 'peak' because the  $|C_n|^2$  vary depending on how the drum head was prepared. In contrast, the frequencies themselves are not characteristic of the preparation process but are properties of the drum head itself; they depend on the eigen-energies of the system, not on how the system is prepared.

This distinction between the characteristic eigenstates of the system with their intrinsic properties and the act of preparing the system in some state that may be a superposition of these eigenstates is essential to keep in mind when applying quantum mechanics to experimental observations.

## V. Operators That Commute and the Experimental Implications

Two hermitian operators that commute

$$[R, S] = RS - SR = 0$$

can be shown to possess complete sets of simultaneous eigenfunctions. That is, one can find complete sets of functions that are eigenfunctions of both R and of S.

The symbol  $[R, S]$  is used to denote what is called the commutator of the operators R and S. There are several useful identities that can be proven for commutators among operators A, B, C, and D, scalar numbers k, and integers n. Several of these are given as follows:

$$\begin{aligned} [A, A^n] &= 0 \\ [kA, B] &= [A, kB] = k[A, B] \\ [A, B+C] &= [A, B] + [A, C] \\ [A+B, C] &= [A, C] + [B, C] \\ [A+B, C+D] &= [A, C] + [A, D] + [B, C] + [B, D] \\ [A, BC] &= [A, B]C + B[A, C] \\ [AB, C] &= [A, C]B + A[B, C] \\ [AB, CD] &= [A, C]DB + C[A, D]B + A[B, C]D + AC[B, D]. \end{aligned}$$

The physical implications of the commutation of two operators are very important because they have to do with what pairs of measurements can be made without interfering with one another. For example, the fact that the x coordinate operator  $\mathbf{x} = x$  and its momentum operator  $\mathbf{p}_x = -i\hbar \frac{\partial}{\partial x}$  do not commute results in the well known Heisenberg uncertainty relationship  $\Delta x \Delta p_x \geq \hbar/2$  involving measurements of  $\mathbf{x}$  and  $\mathbf{p}_x$ .

There are two distinct cases that need to be addressed:

A. If the two operators act on different coordinates (or, more generally, on different sets of coordinates), then they obviously commute. Moreover, in this case, it is straightforward to find the complete set of eigenfunctions of both operators; one simply forms a product of any eigenfunction (say  $f_k$ ) of R and any eigenfunction (say  $g_n$ ) of S. The function  $f_k g_n$  is an eigenfunction of both R and S:

$$R f_k g_n = g_n (R f_k) = g_n (\lambda_k f_k) = \lambda_k f_k g_n ;$$

$$S f_k g_n = f_k (S g_n) = f_k (\mu g_n) = \mu f_k g_n .$$

In these equations use has been made of the fact that  $g_n$  and  $f_k$  are functions of different sets of coordinates that S and R, respectively, act upon.

Product functions such as  $f_k g_n$  yield predictable results when measurements are performed. If the property corresponding to R is measured, the value  $\lambda_k$  is observed, and the wavefunction remains

$f_k g_n$ . If S is measured, the value  $\mu$  is observed, and the wavefunction remains  $f_k g_n$ . For example, the two Hermitian operators  $-i\hbar \frac{\partial}{\partial x}$  and  $-i\hbar \frac{\partial}{\partial r}$  clearly commute. An eigenfunction of

$-i/\hbar$  is of the form  $\exp(ia)$  and an eigenfunction of  $-i/\hbar$  is of the form  $\exp(ibr)$ . The product  $\exp(ia) \exp(ibr)$  is an eigenfunction of both  $-i/\hbar$  and  $-i/\hbar$ . The corresponding eigenvalues are  $a$  and  $b$ , respectively; only these values will be observed if measurements of the properties corresponding to  $-i/\hbar$  and  $-i/\hbar$  are made for a system whose wavefunction is  $\exp(ia) \exp(ibr)$ .

B. If the operators  $R$  and  $S$  act on the same coordinates yet still commute, the implications of their commutation are somewhat more intricate to detail.

As a first step, consider the functions  $\{g_n\}$  that are eigenfunctions of  $S$  with eigenvalues  $\{\mu_n\}$ . Now, act on  $g_n$  with the  $SR$  operator and use the fact that  $SR = RS$  to obtain

$$S R g_n = R S g_n .$$

Because the  $\{g_n\}$  are eigenfunctions of  $S$  having eigenvalues  $\{\mu_n\}$ , this equation further reduces to:

$$S R g_n = R \mu_n g_n = \mu_n R g_n .$$

This is a key result. It shows that the function  $(R g_n)$  is itself either an eigenfunction of  $S$  having the same eigenvalue that  $g_n$  has or it vanishes.

If  $R g_n$  vanishes,  $g_n$  clearly is an eigenfunction of  $R$  (since  $R g_n = 0 g_n$ ) and of  $S$ . On the other hand, if  $R g_n$  is non-vanishing, it must be an eigenfunction of  $S$  having the same eigenvalue ( $\mu_n$ ) as  $g_n$ . If this eigenvalue is non-degenerate (i.e., if  $g_n$  is the only function with eigenvalue  $\mu_n$ ), then  $R g_n$  must be proportional to  $g_n$  itself:

$$R g_n = c_n g_n .$$

This also implies that  $g_n$  is an eigenfunction of both  $R$  and of  $S$ .

Thus far, we can say that functions which are eigenfunctions of  $S$  belonging to non-degenerate eigenvalues must also be eigenfunctions of  $R$ . On the other hand, if the  $\mu_n$  eigenvalue is degenerate (i.e., there are such functions  $g_n, g_n', g_n''$ , etc. that are  $S$ -eigenfunctions with the same  $\mu_n$  as their eigenvalue), all that can be said is that  $R g_n$  is some combination of this  $n$ -fold degenerate manifold of states:

$$R g_n = \sum_{n'} c_{n,n'} g_{n'} .$$

where the sum over  $n'$  runs only over the states with  $S$ -eigenvalues equal to  $\mu_n$ . This same conclusion can be reached no matter which particular state  $g_n$  among the degenerate manifold we begin with. Therefore, the above equation holds for all  $\{g_n\}$  that belong to this degenerate group of states.

The constants  $c_{n,n'}$  form a square (since we act on all states and produce combinations of states) Hermitian (since  $R$  is Hermitian) matrix; in fact,  $c_{n,n'}$  forms the matrix representation of the operator  $R$  within the  $n$ -dimensional space of orthonormal functions  $\{g_n\}$ . As with all Hermitian matrices, a unitary transformation can be employed

to bring it to diagonal form. That is, the orthonormal  $\{g_n\}$  functions can be unitarily combined:

$$G_p = \sum_n U_{p,n} g_n$$

to produce new orthonormal functions  $\{G_p\}$  for which the corresponding matrix elements  $c_{p,p'}$ , defined by

$$\begin{aligned} R G_p &= \sum_n U_{p,n} R g_n = \sum_{n,n'} U_{p,n} c_{n,n'} g_n \\ &= \sum_{p'} \sum_{n,n'} U_{p,n} c_{n,n'} U_{n',p'}^* G_{p'} = \sum_{p'} c_{p,p'} G_{p'} \end{aligned}$$

are diagonal

$$R G_p = c_{p,p} G_p.$$

This shows that the set of functions (the  $G_p$  in this degenerate case) that are eigenfunctions of  $S$  can also be eigenfunctions of  $R$ .

### C. Summary

In summary, we have shown that if  $R$  and  $S$  are operators that act on the same set of coordinates (e.g.,  $-i \hbar / x$  and  $x^2$  or  $\partial^2 / x^2$  and  $-i \hbar / x$ ), then an eigenfunction of  $R$  (denoted  $f_k$  and having eigenvalue  $\epsilon_k$ ) must either (i) be eigenfunction of  $S$  (if its  $R$ -eigenvalue is non-degenerate) or (ii) be a member of a degenerate set of  $R$  eigenfunctions that can be combined among one another to produce eigenfunctions of  $S$ .

An example will help illustrate these points. The  $p_x$ ,  $p_y$  and  $p_z$  orbitals are eigenfunctions of the  $L^2$  angular momentum operator with eigenvalues equal to  $L(L+1) \hbar^2 = 2 \hbar^2$ . Since  $L^2$  and  $L_z$  commute and act on the same (angle) coordinates, they possess a complete set of simultaneous eigenfunctions. Although the  $p_x$ ,  $p_y$  and  $p_z$  orbitals are not eigenfunctions of  $L_z$ , they can be combined (as above) to form the  $G_p$  functions) to form three new orbitals:  $p_0 = p_z$ ,  $p_1 = 2^{-1/2} [p_x + i p_y]$ , and  $p_{-1} = 2^{-1/2} [p_x - i p_y]$  that are still eigenfunctions of  $L^2$  but are now eigenfunctions of  $L_z$  also (with eigenvalues  $0\hbar$ ,  $1\hbar$ , and  $-1\hbar$ , respectively).

It should be mentioned that if two operators do not commute, they may still have some eigenfunctions in common, but they will not have a complete set of simultaneous eigenfunctions. For example, the  $L_z$  and  $L_x$  components of the angular momentum operator do not commute; however, a wavefunction with  $L=0$  (i.e., an S-state) is an eigenfunction of both operators.

### D. Experimental Significance

We use an example to illustrate the importance of two operators commuting to quantum mechanics' interpretation of experiments. Assume that an experiment has been carried out on an atom to measure its total angular momentum  $L^2$ . According to quantum mechanics, only values equal to  $L(L+1) \hbar^2$  will be observed. Further assume, for the



particular experimental sample subjected to observation, that values of  $L^2$  equal to  $2\hbar^2$  and  $0\hbar^2$  were detected in relative amounts of 64 % and 36 % , respectively. This means that the atom's original wavefunction could be represented as:

$$\psi = 0.8 P + 0.6 S,$$

where P and S represent the P-state and S-state components of  $\psi$ . The squares of the amplitudes 0.8 and 0.6 give the 64 % and 36 % probabilities mentioned above.

Now assume that a subsequent measurement of the component of angular momentum along the lab-fixed z-axis is to be measured for that sub-population of the original sample found to be in the P-state. For that population, the wavefunction is now a pure P-function:

$$\psi' = P.$$

However, at this stage we have no information about how much of this  $\psi'$  is of  $m = 1, 0,$  or  $-1$ , nor do we know how much 2p, 3p, 4p, ... np component this state contains.

Because the property corresponding to the operator  $L_z$  is about to be measured, we express the above  $\psi'$  in terms of the eigenfunctions of  $L_z$ :

$$\psi' = P = \sum_{m=1,0,-1} C'_m P_m.$$

When the measurement of  $L_z$  is made, the values  $1\hbar, 0\hbar,$  and  $-1\hbar$  will be observed with probabilities given by  $|C'_1|^2, |C'_0|^2,$  and  $|C'_{-1}|^2$ , respectively. For that sub-population found to have, for example,  $L_z$  equal to  $-1\hbar$ , the wavefunction then becomes

$$\psi'' = P_{-1}.$$

At this stage, we do not know how much of 2p<sub>-1</sub>, 3p<sub>-1</sub>, 4p<sub>-1</sub>, ... np<sub>-1</sub> this wavefunction contains. To probe this question another subsequent measurement of the energy (corresponding to the  $H$  operator) could be made. Doing so would allow the amplitudes in the expansion of the above  $\psi'' = P_{-1}$

$$\psi'' = P_{-1} = \sum_n C''_n nP_{-1}$$

to be found.

The kind of experiment outlined above allows one to find the content of each particular component of an initial sample's wavefunction. For example, the original wavefunction has

0.64  $|C''_n|^2 |C'_m|^2$  fractional content of the various  $nP_m$  functions.

Let us consider another experiment in which an initial sample (with wavefunction  $\psi$ ) is first subjected to measurement of  $L_z$  and then subjected to measurement of  $L^2$  and then of the energy. In this order, one would first find specific values (integer multiples of  $\hbar$ ) of  $L_z$  and one would express  $\psi$  as

$$\psi = \sum_m D_m \psi_m.$$

At this stage, the nature of each  $\psi_m$  is unknown (e.g., the  $\psi_1$  function can contain  $n p_1$ ,  $n' d_1$ ,  $n'' f_1$ , etc. components); all that is known is that  $\psi_m$  has  $m \hbar$  as its  $L_z$  value.

Taking that sub-population ( $|D_m|^2$  fraction) with a particular  $m \hbar$  value for  $L_z$  and subjecting it to subsequent measurement of  $L^2$  requires the current wavefunction  $\psi_m$  to be expressed as

$$\psi_m = \sum_L D_{L,m} \psi_{L,m}.$$

When  $L^2$  is measured the value  $L(L+1) \hbar^2$  will be observed with probability  $|D_{m,L}|^2$ , and the wavefunction for that particular sub-population will become

$$\psi'' = \psi_{L,m}.$$

At this stage, we know the value of  $L$  and of  $m$ , but we do not know the energy of the state. For example, we may know that the present sub-population has  $L=1$ ,  $m=-1$ , but we have no knowledge (yet) of how much  $2p_{-1}$ ,  $3p_{-1}$ , ...  $np_{-1}$  the system contains.

To further probe the sample, the above sub-population with  $L=1$  and  $m=-1$  can be subjected to measurement of the energy. In this case, the function  $\psi_{1,-1}$  must be expressed as

$$\psi_{1,-1} = \sum_n D_n'' n P_{-1}.$$

When the energy measurement is made, the state  $n P_{-1}$  will be found  $|D_n''|^2$  fraction of the time.

We now need to explain how the fact that  $L_z$ ,  $L^2$ , and  $H$  all commute with one another (i.e., are mutually commutative) makes the series of measurements described above more straightforward than if these operators did not commute. In the first experiment, the fact that they are mutually commutative allowed us to expand the 64 % probable  $L^2$  eigenstate with  $L=1$  in terms of functions that were eigenfunctions of the operator for which measurement was about to be made without destroying our knowledge of the value of  $L^2$ . That is, because  $L^2$  and  $L_z$  can have simultaneous eigenfunctions, the  $L=1$  function can be expanded in terms of functions that are eigenfunctions of both  $L^2$  and  $L_z$ . This in turn, allowed us to find experimentally the sub-population that had, for example a  $-1 \hbar$  value of  $L_z$  while retaining knowledge that the state remains an eigenstate of  $L^2$  (the state at this time had  $L=1$  and  $m=-1$  and was denoted  $P_{-1}$ ) Then, when this  $P_{-1}$  state was subjected to energy measurement, knowledge of the energy of the sub-population could be gained without giving up knowledge of the  $L^2$  and  $L_z$  information; upon carrying out said measurement, the state became  $n P_{-1}$ .

In contrast, if (hypothetically)  $L^2$  and  $L_z$  did not commute, the  $L=1$  function originally detected with 64 % probability would be altered by the subsequent  $L_z$  measurement in a manner that destroys our knowledge of  $L^2$ . The  $P$  function could still have been expanded in terms of the eigenfunctions of the property about to be probed ( $L_z$ )

$$P = \sum_{m=1,0,-1} C'_m \psi_m.$$

However, because  $L^2$  and  $L_z$  do not commute in this hypothetical example, the states  $\psi_m$  that are eigenfunctions of  $L_z$  will not, in general, also be eigenfunctions of  $L^2$ . Hence, when  $L_z$  is measured and a particular value (say  $-1\hbar$ ) is detected, the wavefunction becomes

$$\psi' = \psi_{-1},$$

which is no longer an eigenfunction of  $L^2$ .

The essential observations to be made are:

1. After the first measurement is made (say for operator R), the wavefunction becomes an eigenfunction of R with a well defined R-eigenvalue (say  $r$ ):  $\psi = \psi(r)$ .

2. The eigenfunctions of the second operator S (i.e., the operator corresponding to the measurement about to be made) can be taken to also be eigenfunctions of R if R and S commute. This then allows  $\psi(r)$  to be expanded in terms of functions that are both R-eigenfunctions (with eigenvalue  $r$ ) and S-eigenfunctions (with various eigenvalues  $\mu_n$ ):

$\psi(r) = \sum_n C_n \psi(r, \mu_n)$ . Upon measurement of S, the wavefunction becomes one of these  $\psi(r, \mu_n)$  functions. When the system is in this state, both R- and S- eigenvalues are known precisely; they are  $r$  and  $\mu_n$ .

3. The eigenfunctions of the second operator S (i.e., the operator corresponding to the measurement about to be made) can not be taken to also be eigenfunctions of R if R and S do not commute. The function  $\psi(r)$  can still be expanded in terms of functions that are both S-eigenfunctions (with various eigenvalues  $\mu_n$ ):  $\psi(r) = \sum_n C_n \psi(\mu_n)$ . However, because R and S do not commute, these  $\psi(\mu_n)$  functions are not, in general, also R-eigenfunctions; they are only S-eigenfunctions. Then, upon measurement of S, the wavefunction becomes one of these  $\psi(\mu_n)$  functions. When the system is in this state, the S- eigenvalue is known precisely; it is  $\mu_n$ . The R-eigenvalue is no longer specified. In fact, the new state  $\psi(\mu_n)$  may contain components of all different R-eigenvalues, which can be represented by expanding  $\psi(\mu_n)$  in terms of the R-eigenfunctions:  $\psi(\mu_n) = \sum_k D_k \psi(r_k)$ . If R were measured again, after the state has been prepared in  $\psi(\mu_n)$ , the R-eigenvalues  $\{r_k\}$  would be observed with probabilities  $\{|D_k|^2\}$ , and the wavefunction would, for these respective sub-populations, become  $\psi(r_k)$ .

It should now be clear that the act of carrying out an experimental measurement disturbs the system in that it causes the system's wavefunction to become an eigenfunction of the operator whose property is measured. If two properties whose corresponding operators commute are measured, the measurement of the second property does not destroy knowledge of the first property's value gained in the first measurement. If the two properties do not commute, the second measurement does destroy knowledge of the first property's value. It is thus often said that 'measurements for operators that do not commute interfere with one another'.