

CHE-2H45 QUANTUM MECHANICS AND SYMMETRY

BASIC QUANTUM MECHANICS

9 Lecture/Workshops by Professor David L. Andrews

SUMMARY

Introduction; Principles of quantum mechanics; Operators and observables; The time-dependent Schrödinger equation, stationary states and transitions; Angular momentum in quantum mechanics; The harmonic oscillator and its applications in chemistry; Anharmonic vibrations and molecular inversion: Perturbation theory.

READING LIST

This set of lectures is designed to be largely self-contained. You may, however, find the following book especially helpful:

Molecular Quantum Mechanics, by P. W. Atkins and R. S. Friedman (Oxford University Press).

INTRODUCTION

Modern chemistry is firmly based on the concept of atoms and molecules as structural entities, and a very important part of chemical physics consists of experiments designed for material characterization and molecular structure determination. For the great majority of such experiments, and particularly for those based upon spectroscopic techniques, the interpretation of results is based upon quantum mechanics. Thus quantum mechanics plays a vital role not only in the description of atomic and molecular physics, but also in the evaluation of results from a wide range of experimental methods. The introductory lecture course is designed to provide a detailed introduction to the concepts and methods most relevant to chemical and physical applications, particularly to the interpretation of spectra.

It is important to develop an understanding of the place of the theory within the framework of the rest of science. Quantum mechanics is quite distinct from earlier quantum theory, which was centred upon the wavelengths and frequencies of light absorbed or emitted in atomic transitions. The Planck relation, $\Delta E = h\nu$, first established a simple relationship between the frequency ν of optical radiation and a difference in energy, ΔE , between the discrete states involved in an atomic transition. Einstein's treatment of the photoelectric effect incorporated the same quantum energy in the relation $T = h\nu - \phi$ for the kinetic energy T of each released photoelectron (ϕ being the surface work function). Quantum mechanics, however, which leads to our present understanding of electron wavefunctions and molecular orbitals, is built upon a much broader base of assertions about the way the physical world operates. Because of this, it is a theory that has extraordinarily wide significance, extending to issues such as human consciousness and morality.

We shall begin by looking in detail at the foundations upon which quantum mechanics is built, known as the Postulates of Quantum Mechanics. Self-consistent but unproven, they nevertheless provide a basis for constructing all the detailed applications which prove so hugely successful, producing results that agree with experiment and making predictions that also prove correct. In this respect they have a similar status to Newton's Laws of Motion in classical physics.

THE POSTULATES OF QUANTUM MECHANICS

There are several fundamental postulates, and they can be expressed in many different ways. I like the statements given in an old book by I. N. Levine called *Quantum Chemistry*, which in a marginally modified form are as shown on the handout. In general the wavefunction ψ is complex, but according to the *Born interpretation*, its physical significance lies in the representation of a probability density by the quantity $|\psi|^2$. So since total probability must amount to unity, we have;

$$\int |\psi|^2 d\tau = 1$$

This is known as the *normalisation condition* on the wavefunction.

Postulate 1 The state of any system is described by a function ψ of the particle coordinates and time. This function, called the *wavefunction* state function (or state function) contains all the information that can be determined about the system. It is further postulated that ψ is single-valued, continuous, and quadratically integrable.

Postulate 2 To every physical observable there corresponds a linear Hermitian operator. To find this operator, the classical-mechanical expression for the observable is written down in terms of Cartesian coordinates and corresponding linear momentum components; then each coordinate x is replaced by the operator $x \times$, and each momentum component p_x by the operator $-i\hbar \partial/\partial x$.

Postulate 3 The only possible values that can result from measurements of a physical observable G , say, are the eigenvalues g_i of the equation

$$\hat{G}\psi_i = g_i\psi_i$$

where the operator corresponds to the property G . The eigenfunctions ψ are required to be well-behaved.

Postulate 4 The eigenfunctions of any linear Hermitian operator representing a physical observable form a complete set.

Postulate 5 If ψ is the normalised state function of a system at a given time, then the average value of a physical observable at that time (the *expectation value*) is given by;

$$\langle G \rangle = \int \psi^* \hat{G} \psi d\tau$$

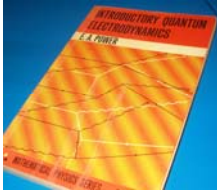
Postulate 6 The time development of the state of an undisturbed system is given by the time-dependent Schrödinger equation

$$i\hbar \frac{\delta\psi}{\delta t} = \hat{H}\psi$$

where \hat{H} , known as the *Hamiltonian*, is the energy operator.

To proceed further we shall need to master some simple mathematics.

OPERATOR ALGEBRA



Consider a quantum mechanical 'ket' representation of the state of a book $|\text{book}\rangle$. Various things can be done with it, represented by quantum operators (designated with a 'carat' or 'hat', $\hat{}$)

You can read it – operator \hat{R} .

The output of this 'measurement' is the subject matter λ ;

$$\hat{R}|\text{book}\rangle = \lambda|\text{book}\rangle$$



You can take an X-ray photograph of it – operator \hat{X} .
The output of this 'measurement' is the structural image φ ;

$$\hat{X}|\text{book}\rangle = \varphi|\text{book}\rangle$$

★ Remember, an operator always operates to its *right*.

When two operations are performed, the sequence can matter in some case, though not in others. Consider these two:

$$\hat{R}\hat{X}|\text{book}\rangle = \hat{R}\varphi|\text{book}\rangle = \lambda\varphi|\text{book}\rangle$$

$$\begin{aligned}\hat{X}\hat{R}|\text{book}\rangle &= \hat{X}\lambda|\text{book}\rangle = \varphi\lambda|\text{book}\rangle \\ &= \lambda\varphi|\text{book}\rangle\end{aligned}$$

$$\left. \begin{aligned}\therefore \hat{R}\hat{X}|\text{book}\rangle &= \hat{X}\hat{R}|\text{book}\rangle \\ \therefore (\hat{R}\hat{X} - \hat{X}\hat{R})|\text{book}\rangle &= 0\end{aligned} \right|$$

$$[\hat{R}, \hat{X}] \equiv (\hat{R}\hat{X} - \hat{X}\hat{R}) = 0$$

We call $[\hat{R}, \hat{X}]$ the **commutator** of \hat{R} and \hat{X} , and if it is zero we say the operators **commute**.

$|\text{book}\rangle$ is an **eigenstate** of both operators \hat{R} and \hat{X} , and so these operators do commute



But consider, you can also burn the book – operator \hat{B} . The output of this ‘measurement’ is just ashes!

$$\hat{B}|\text{book}\rangle = |\text{ashes}\rangle$$

So $|\text{book}\rangle$ is not an eigenstate of \hat{B} . Combining the operations \hat{B} and \hat{R} for example, we have;

$$\begin{aligned} \hat{B}\hat{R}|\text{book}\rangle &= \hat{B}\lambda|\text{book}\rangle = \lambda|\text{ashes}\rangle \\ &\neq \hat{R}\hat{B}|\text{book}\rangle \end{aligned}$$

Thus $[\hat{R}, \hat{B}] \neq 0$

Burning and reading are operations that do not commute.

OPERATORS AND COMMUTATORS

The concept of commutation relates to the fact that, although different operators are additive such that $\hat{M} + \hat{N}$ gives the same result as $\hat{N} + \hat{M}$, their product can often give a different result according to the order of operation. If for example \hat{O}_1 and \hat{O}_2 are operators corresponding to different dynamical variables of a particular system, we define their commutator as:

$$[\hat{O}_1, \hat{O}_2] = \hat{O}_1\hat{O}_2 - \hat{O}_2\hat{O}_1$$

For example take the operators x and d/dx ; what is the commutator $[x, d/dx]$? Now because the commutator involves only operators and is itself therefore an operator, it is easiest to see what this means if we apply it to some unspecified function, say ψ ,

$$\left[x, \frac{d}{dx} \right] \psi = x \frac{d\psi}{dx} - \frac{d}{dx} (x\psi) = x \frac{d\psi}{dx} - \left(\psi + x \frac{d\psi}{dx} \right) = -\psi$$

In operator form, since the above result is valid for any function ψ , then we have;

$$\left[x, \frac{d}{dx} \right] = -1.$$

Class Exercises

1. For the function $\phi = a \sin x + bx^3$ determine the result of the operations $\hat{M}\phi$, $\hat{N}\phi$ and $\hat{p}_x\phi$, where;

$$\hat{M} = 3 \frac{d}{dx}; \quad \hat{N} = 2i - 5g \frac{d}{dx^2}; \quad \hat{p}_x = -i\hbar \frac{d}{dx}.$$

2. For the function $\psi = ax \sin x + bx$, determine the results $\hat{M}\hat{N}\psi$ and $\hat{N}\hat{M}\psi$.

3. Write down the explicit form of the quantum mechanical operators for position and momentum in the x -direction, \hat{x} and \hat{p}_x respectively. Work out their commutator $[\hat{x}, \hat{p}_x]$, by applying it to an arbitrary function f . Comment on the physical significance of the result, and state which quantum principle it illustrates.
4. Work out the result of the following commutators:

$$[\hat{p}_x, [\hat{x}, \hat{p}_x]] \text{ and } [\hat{p}_x, [\hat{x}^2, \hat{p}_x]].$$

EIGENFUNCTIONS AND EIGENVALUES

In general, quantum mechanical operators are formed according to the prescription of postulate 2. Let us focus on a special kind of operator equation, of the form:

$$\hat{G}\phi = g\phi$$

in which the carat denotes an operator. This is a general equation of the class to which the Schrödinger equation obviously belongs. In general a function such as ϕ which, when operated on by a particular operator gives just a multiplier g times itself, is termed an *eigenfunction* of that operator. The multiplier g is termed the corresponding *eigenvalue*. For example the wavefunction e^{ikx} is an eigenfunction of the quantum mechanical momentum operator $-i\hbar \frac{d}{dx}$ with eigenvalue $\hbar k$.

It is very significant that, although the operator and the wavefunction in the above example are both complex, the momentum eigenvalue is *real*. In fact we shall see that operators represent acts of measurement, and therefore all operators corresponding to physical observables have real eigenvalues. Such operators are called *Hermitian* (after Charles Hermite, a French mathematician).



Hermitian operators have to satisfy the equation;

$$\int \varphi^* \hat{G} \psi dx = \int (\hat{G} \varphi)^* \psi dx$$

Although the above equation appears a bit abstract, it does lead to some important results, as we shall see later. Notice that the order here is important, because on the left the operator acts upon ψ and on the right upon φ . It is readily proven that the eigenvalues associated with eigenfunctions of a Hermitian operator have to be real, as should obviously be the case if they represent values for a real observable. For example both the momentum operator and the Hamiltonian operator are Hermitian since they correspond to the real physical observables of momentum and energy.

DIRAC BRACKET NOTATION

Frequently in quantum mechanics we encounter integrals of the kind appearing above. A shorthand bracket notation due to Paul Dirac writes these as follows:

$$\langle \varphi | \hat{G} | \psi \rangle \equiv \int \varphi^* \hat{G} \psi dx$$

Corny though it sounds, the left- and right-hand ends of the expression are referred to as the 'bra' and 'ket' respectively. Whenever a complete bra(c)ket appears, integration is taken for granted. The normalization of a wavefunction ψ , for example, is simply written as;

$$\langle \psi | \psi \rangle = 1$$

Note that when there is a set of wavefunctions ϕ_i (such as correspond to the various states of a hydrogen atom, for example), where the label ' i ' is a quantum number or numbers designating a particular member of the set, we may just write the label in the 'bra' and 'ket' as a further simplification of notation, e.g.

$$\langle i | \hat{A} | j \rangle \equiv \langle \phi_i | \hat{A} | \phi_j \rangle \equiv \int \phi_i^* \hat{A} \phi_j dx$$



QUANTUM MEASUREMENTS

Following on from Postulate 3, we can now address some matters concerning the quantum theory of measurement. The significance of operator commutation is as follows:

If a system in a given state is to have exact values for two different physical observables, the corresponding operators must commute.

We can easily prove this since the only exact values we can obtain are eigenvalues of the operators. Suppose we consider a state $|\phi\rangle$ whose wavefunction is an eigenfunction of two operators \hat{F} and \hat{G} , with eigenvalues f and g respectively. We can write;

$$\hat{F}|\phi\rangle = f|\phi\rangle \text{ and } \hat{G}|\phi\rangle = g|\phi\rangle$$

$$\therefore \hat{F}\hat{G}|\phi\rangle = \hat{F}(\hat{G}|\phi\rangle) = \hat{F}(g|\phi\rangle) = g\hat{F}|\phi\rangle = gf|\phi\rangle;$$

$$\hat{G}\hat{F}|\phi\rangle = \hat{G}(\hat{F}|\phi\rangle) = \hat{G}(f|\phi\rangle) = f\hat{G}|\phi\rangle = fg|\phi\rangle$$

$$\therefore \hat{F}\hat{G}|\phi\rangle - \hat{G}\hat{F}|\phi\rangle = 0 \quad \therefore (\hat{F}\hat{G} - \hat{G}\hat{F})|\phi\rangle = 0 \quad \therefore [\hat{F}, \hat{G}] = 0$$

This means that the two dynamical variables corresponding to the two operators can only be simultaneously measured if the operators themselves commute. For example, the case of position and momentum (*Class Exercise 3*) illustrates Heisenberg's Uncertainty Relation; we are not able to simultaneously obtain exact values for both these variables from any system. In the case of energy and angular momentum, however, it can be shown that the appropriate operators do commute, and that is why in describing atomic and molecular states both energy and angular momentum can be simultaneously specified.

Generally, any given operator will have a number of different eigenfunctions, each associated with a different eigenvalue (e.g. various wavefunctions, each with a different energy). We can pose the question: is there any relationship between different eigenfunctions of the same operator? To take this further, we note that in Dirac notation

a Hermitian operator \hat{G} satisfies the relation $\langle \phi | \hat{G} | \psi \rangle = \langle \psi | \hat{G} | \phi \rangle^*$ (exactly equivalent to the relationship in the box on page 8). To press the point, we can be specific and consider the implications of the Hamiltonian operator being Hermitian (which it must be, simply because it represents energy, a physical observable; accordingly its eigenvalues are real).

Consider two states with different energies,

$$\hat{H} |\phi_1\rangle = E_1 |\phi_1\rangle \text{ and } \hat{H} |\phi_2\rangle = E_2 |\phi_2\rangle$$

Forming a Dirac bracket;

$$\langle \phi_1 | \hat{H} | \phi_2 \rangle = \langle \phi_1 | E_2 | \phi_2 \rangle = E_2 \langle \phi_1 | \phi_2 \rangle.$$

Because the Hamiltonian is Hermitian, the above result must be the same as we get from:

$$\langle \phi_2 | \hat{H} | \phi_1 \rangle^* = \langle \phi_2 | E_1 | \phi_1 \rangle^* = E_1^* \langle \phi_2 | \phi_1 \rangle^* = E_1 \langle \phi_1 | \phi_2 \rangle.$$

$$\therefore (E_2 - E_1) \langle \phi_1 | \phi_2 \rangle = 0. \text{ Since we specified } E_2 \neq E_1 \text{ it follows that } \langle \phi_1 | \phi_2 \rangle = 0.$$

The above example illustrates what is known as the principle of *orthogonality*. In general we conclude that:

Eigenfunctions of the same Hermitian operator with different eigenvalues are orthogonal, in the sense that $\langle \phi_i | \phi_j \rangle = 0$ if $i \neq j$

What is the physical significance of this result? In fact it is the origin of energy and angular momentum conservation in the formalism of quantum mechanics. For example if ϕ_1 and ϕ_2 in the above example were not orthogonal, a system initially in one state could drift into the other state with a different energy, violating energy conservation.

In the light of Postulate 4 it also means that any function of the same variables can be uniquely expressed in terms of the complete set of functions – just as the geometric orthogonality of x , y and z unit vectors means that we can unambiguously represent any point in 3D space by a linear combination of those vectors. So for example, even the

wavefunction for a very disturbed molecule is expressible in terms of unperturbed states – the usual solutions to Schrödinger's equation.

In Dirac notation the general orthogonality result can be neatly combined with the normalization condition as $\langle \phi_i | \phi_j \rangle = \delta_{ij}$, where the term on the right is the Kronecker delta (zero if $i \neq j$ but unity if $i = j$).

Class Exercises

5. Write down in the simplest form of Dirac notation an expression of the orthonormality of a set of states ϕ_i .
6. Write down in Dirac notation the eigenvalue equation for states ϕ_i , eigenfunctions of an operator \hat{A} with associated eigenvalues a_i .
7. Write down the Dirac bracket for the expectation value of an operator \hat{A} for a system with an arbitrary wavefunction ψ . Show that if the system is in one of the states ϕ_i referred to in question 6, then the expectation value is the same as the eigenvalue.

Example of an application. Write down the expansion postulate in Dirac notation. Using the class exercise results find an expression, in terms of the eigenvalues a_i , for the expectation value of an operator \hat{A} , when the wavefunction ψ is not an eigenstate of that operator.

The wavefunction ψ can be expressed as a linear combination of the basis set, say ϕ_i ;

$$|\psi\rangle = \sum_i c_i |\phi_i\rangle, \text{ which also implies that } \langle\psi| = \sum_j c_j^* \langle\phi_j|$$

The required expectation value is thus:

$$\begin{aligned} \langle\psi|\hat{A}|\psi\rangle &= \sum_i \sum_j c_j^* c_i \langle\phi_j|\hat{A}|\phi_i\rangle = \sum_i \sum_j c_j^* c_i \langle\phi_j|a_i|\phi_i\rangle \\ &= \sum_i \sum_j c_j^* c_i a_i \langle\phi_j|\phi_i\rangle = \sum_i \sum_j c_j^* c_i a_i \delta_{ij} = \sum_i c_i^* c_i a_i = \sum_i |c_i|^2 a_i \end{aligned}$$

The result, based on Postulate 5, signifies a weighted average of the values that would be determined in each if the states i , hence:

$|c_i|^2$ signifies the probability of finding the system in the state $|\phi_i\rangle$.

Read about Schrödinger's cat!

We have come to the last of the Postulates of Quantum Mechanics, which gives *the Schrödinger equation* in a form that may be new to you. The given result is perfectly general; to recover the more familiar form we must suppose that the Hamiltonian operator \hat{H} is not explicitly dependent on time. This only means that the energy of the system does not vary, in other words our system is a closed one. It is then possible to factorise the time-dependence of the wavefunction as:

$$|\Psi(\mathbf{r}, t)\rangle = |\psi(\mathbf{r})\rangle |\theta(t)\rangle$$

$$\therefore \hat{H}(\mathbf{r})|\psi(\mathbf{r})\rangle |\theta(t)\rangle = i\hbar \frac{\partial}{\partial t} |\psi(\mathbf{r})\rangle |\theta(t)\rangle$$

$$\therefore |\theta(t)\rangle \hat{H}(\mathbf{r})|\psi(\mathbf{r})\rangle = |\psi(\mathbf{r})\rangle i\hbar \frac{\partial}{\partial t} |\theta(t)\rangle$$

Now dividing through by $|\psi(\mathbf{r})\rangle |\theta(t)\rangle$;

$$\frac{1}{|\psi(\mathbf{r})\rangle} \hat{H}(\mathbf{r})|\psi(\mathbf{r})\rangle = i\hbar \frac{1}{|\theta(t)\rangle} \frac{\partial}{\partial t} |\theta(t)\rangle$$

Since in the last line the left-hand side involves only spatial coordinates, while the right-hand side involves only time, the only way the two sides can invariably equate with each other is if each is a constant, say E . So we obtain two separate equations;

$$\frac{1}{|\psi(\mathbf{r})\rangle} \hat{H}(\mathbf{r})|\psi(\mathbf{r})\rangle = E, \quad \therefore \boxed{\hat{H}(\mathbf{r})|\psi(\mathbf{r})\rangle = E|\psi(\mathbf{r})\rangle}$$

$$i\hbar \frac{1}{|\theta(t)\rangle} \frac{\partial}{\partial t} |\theta(t)\rangle = E, \quad \therefore |\theta(t)\rangle = e^{-iEt/\hbar}$$

The first (highlighted) equation is of course the usual *time-independent* Schrödinger equation. The relationship below it signifies that each spatial wavefunction $|\psi(\mathbf{r})\rangle$ carries a time-dependent phase factor $e^{-iEt/\hbar}$, one which disappears in the probability density, since $\Psi^* \Psi = (\psi^* e^{iEt/\hbar})(\psi e^{-iEt/\hbar}) = \psi^* \psi$. Since time drops out of this, and any other measurement, we regard this as denoting a *stationary state* of the system.

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PROBLEMS ON OPERATORS

1. Write down two equations to represent the fact that a given wavefunction is simultaneously an eigenfunction of two different Hermitian operators. What conclusion can be drawn about these operators?
2. Write down two equations to represent the fact that two different wavefunctions are simultaneously eigenfunctions of the same Hermitian operator, with different eigenvalues. What conclusion can be drawn about these wavefunctions?
3. Resolve the following commutator: $\left[\frac{d^2}{dx^2}, ax^2 + bx + c \right]$.
4. Evaluate $\left[x \frac{d}{dx}, x^2 \frac{d}{dx} \right]$.

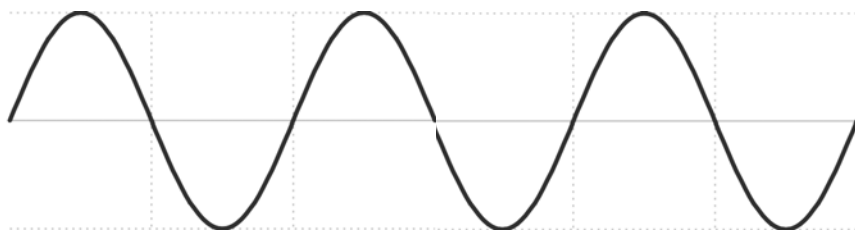
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Answers

1. *The operators commute.*
2. *The wavefunctions are orthogonal.*
3. $2a + 2(2ax + b) \frac{d}{dx}$.
4. 0.

THE SIMPLE HARMONIC OSCILLATOR

With the tools we now have at our disposal, we can in principle tackle any problem. A very useful and informative example is the case of simple harmonic motion, a type of behaviour that arises in a huge number of systems in chemistry and physics – for example in molecular vibrations, the thermal properties of crystals, and the quantum theory of light. Photons themselves are a form of simple harmonic motion – their electric and magnetic fields follow a sine wave.



What we shall find, is that we can solve the Schrödinger equation for any such system, just by using simple operator algebra, without even needing to find the wavefunctions.

Let us start with the classical energy expression,

$$E_{\text{classical}} = \frac{1}{2}mv^2 + \frac{1}{2}kx^2 ,$$

where we are assuming back and forth motion of a particle in the x -direction, about the origin $x = 0$, with v being the velocity and m the particle mass; k is the force constant. Our first task is to determine the quantum mechanical Hamiltonian, by converting the above expression into quantum operator form. We don't have an operator for velocity but we do for momentum, and so using $p_x = mv$ we first rewrite the above as;

$$E_{\text{classical}} = \frac{p_x^2}{2m} + \frac{1}{2}kx^2 .$$

Now from Postulate 2 we substitute the operator for momentum in the x -direction (and the position variable x doesn't change) so that we find;

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m\omega^2 x^2$$

In the last step, we have used the relationship for the classical circular frequency of oscillation, $\omega = \sqrt{k/m}$.

From here onwards, we drop the carat over the H since we shall never use that symbol for anything other than the Hamiltonian operator. Now clearly the Hamiltonian has the general form of a sum of two terms, one quadratic in momentum and the other, quadratic in position. For convenience we can write H in terms of two new operators P and Q ;

$$H = (P^2 + Q^2) \hbar\omega,$$

where the $\hbar\omega$ has the units of energy so that both P and Q are dimensionless. Explicitly, we can have;

$$P = -i\sqrt{\frac{\hbar}{2m\omega}} \frac{d}{dx}; \quad Q = \sqrt{\frac{m\omega}{2\hbar}} x$$

We can easily find out the commutation properties of our two operators P and Q ;

$$[P, Q] = -\frac{i}{2} \left[\frac{d}{dx}, x \right] = -\frac{i}{2}$$

The result can immediately be used to rewrite the Hamiltonian in another form, since we can now write;

$$\begin{aligned} P^2 + Q^2 &= (P^2 + Q^2 + iQP - iPQ + iPQ - iQP) \\ &= (P + iQ)(P - iQ) + i[P, Q] = (P + iQ)(P - iQ) + \frac{1}{2} \end{aligned}$$

For an even more convenient shorthand we can introduce two new operators, defined as;

$$a = P - iQ; \quad a^+ = P + iQ$$

so that the Hamiltonian eventually becomes expressible as:

$$H = \left(a^+ a + \frac{1}{2} \right) \hbar \omega$$

In the following, we shall need nothing more than this result, and the commutation relation for a and a^+ , which is easily found.

Class Exercise

8. Prove that $[a, a^+] = 1$

To proceed, we can reason that the solutions to the time-independent Schrödinger equation are expressible as;

$$H|n\rangle = E_n|n\rangle$$

which really just says that the wavefunctions can be labeled by some quantum number n , though as yet we know nothing about the possible values of those numbers.

We also don't know the result of operating either a or a^+ on the states $|n\rangle$. However, we can get further by investigating the properties of the results of such operations. Consider first $a|n\rangle$; what happens if we operate upon it by the Hamiltonian operator? We shall have;

$$Ha|n\rangle = \left(a^+ a + \frac{1}{2} \right) \hbar \omega a|n\rangle = \left(a^+ a a + \frac{1}{2} a \right) \hbar \omega |n\rangle$$

Using the only other information we have – the commutation relation – we can write;

$$a^+ a a = \left(a a^+ - 1 \right) a = a a^+ a - a$$

So, we get;

$$\begin{aligned}
Ha|n\rangle &= \left(aa^+a - a + \frac{1}{2}a\right)\hbar\omega|n\rangle = \left(aa^+a - \frac{1}{2}a\right)\hbar\omega|n\rangle \\
&= a\left(a^+a - \frac{1}{2}\right)\hbar\omega|n\rangle = a(H - \hbar\omega)|n\rangle
\end{aligned}$$

where, in the last step, we have again used our knowledge of the Hamiltonian. Hence;

$$\begin{aligned}
Ha|n\rangle &= aH|n\rangle - a\hbar\omega|n\rangle = aE_n|n\rangle - a\hbar\omega|n\rangle \\
&= E_n a|n\rangle - \hbar\omega a|n\rangle = (E_n - \hbar\omega)a|n\rangle.
\end{aligned}$$

Interpreting the result, we now know that:

$a|n\rangle$ is an eigenfunction of the Hamiltonian H with energy eigenvalue $(E_n - \hbar\omega)$.

It proves interesting to apply the result to the ground state – since there has to be one – which we can label as $|0\rangle$;

$$Ha|0\rangle = (E_0 - \hbar\omega)a|0\rangle.$$

But if we assume the result of the operation $a|0\rangle$ is non-zero, the above result does make sense – it implies that there would have to be an eigenstate of H with energy $E_0 - \hbar\omega$, obviously less than E_0 . This would be logically inconsistent – we said that the state with lowest energy is $|0\rangle$. Since the result of assuming that $a|0\rangle$ is non-zero proves to be nonsense, the premise must be wrong. Therefore we must conclude that;

$$a|0\rangle = 0.$$

Class Exercise

Use the above result, together with the highlighted equation on p. 16, to determine the ground state energy of the simple harmonic oscillator.

From the Schrödinger equation we have;

$$\begin{aligned} H|0\rangle &= \left(a^+a + \frac{1}{2}\right)\hbar\omega|0\rangle = a^+(\hbar\omega)a|0\rangle + \frac{1}{2}\hbar\omega|0\rangle \\ &= 0 + \frac{1}{2}\hbar\omega|0\rangle = \frac{1}{2}\hbar\omega|0\rangle \end{aligned}$$

But, since obviously $H|0\rangle = E_0|0\rangle$, we can conclude that:

The energy E_0 of the ground state is $\frac{1}{2}\hbar\omega$

Class exercise

Applying similar methods to those used for $a|n\rangle$, prove that:

$$Ha^+|n\rangle = (E_n + \hbar\omega)a^+|n\rangle.$$

$a^+|n\rangle$ is an eigenfunction of the Hamiltonian H with energy eigenvalue $(E_n + \hbar\omega)$

Now suppose we apply the last result to the ground state;

$$Ha^+|0\rangle = (E_0 + \hbar\omega)a^+|0\rangle.$$

This means there is a state, obtained by the operation $a^+|0\rangle$, with energy $E_0 + \hbar\omega = \frac{3}{2}\hbar\omega$. Indeed if we apply a^+ to that state, we shall find another state of energy $\frac{5}{2}\hbar\omega$. It is easy to see that if we keep going we shall discover a whole series of states with energies of the general form;

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

In fact, just by playing around with the operators, we have obtained the energies of the entire set of states for the simple harmonic oscillator without even needing the wavefunctions. Also, we now know that

$$H|n\rangle = E_n|n\rangle \Rightarrow \left(a^+a + \frac{1}{2}\right)\hbar\omega|n\rangle = \left(n + \frac{1}{2}\right)\hbar\omega|n\rangle \therefore a^+a|n\rangle = n|n\rangle$$

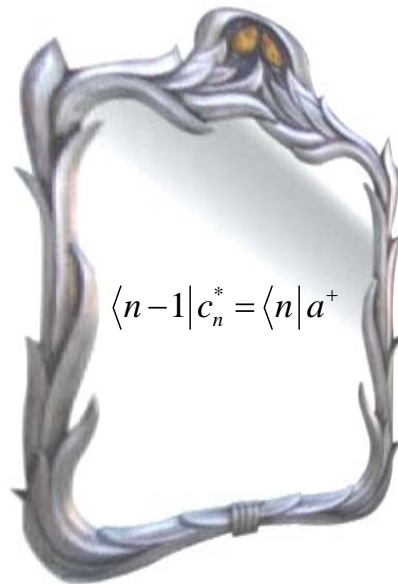
The product operator a^+a is sometimes known as the *number operator*.

It now remains to find out what we actually get from the operations $a|n\rangle$ and $a^+|n\rangle$. Consider the first; we now know that the result is an eigenstate of the Hamiltonian with an energy $E_n - \hbar\omega$ that is in fact equal to that of the state with quantum number $n - 1$. We can therefore conclude that the result $a|n\rangle$ is a state that must be identifiable with $|n-1\rangle$, at least to within a (possibly complex) proportionality factor c ;

$a|n\rangle = c|n-1\rangle$. For this reason a is known as the *lowering operator*.

To find c , we use the result of Hermitian conjugation.

HERMITIAN CONJUGATION



$$\langle n-1|c_n^* = \langle n|a^+ \quad a|n\rangle = c_n|n-1\rangle$$

Putting the sides together to complete the Dirac brackets, we then have;

$$\langle n|a^+a|n\rangle = \langle n-1|c^*c|n-1\rangle$$

$$\therefore \langle n|n|n\rangle = \langle n-1||c|^2|n-1\rangle \Rightarrow n\langle n|n\rangle = |c|^2 \langle n-1|n-1\rangle \therefore n = |c|^2$$

We can in fact choose c to be real, and hence with $c = \sqrt{n}$ we have;

$$a|n\rangle = \sqrt{n}|n-1\rangle.$$

CHE-2H45 QUANTUM MECHANICS AND SYMMETRY

PROBLEMS ON THE SIMPLE HARMONIC OSCILLATOR

- Using similar methods to those used in dealing with the lowering operator, determine the value of d in the equation

$$a^+ |n\rangle = d |n+1\rangle$$

- Determine the results of each of the following operations of raising and lowering operators, a^+ and a respectively, on simple harmonic oscillator states $|n\rangle$;

$$a^+ a |n\rangle, \quad a a^\dagger |n\rangle, \quad a^+ a^+ a a |n\rangle, \quad \langle n | a^+ a a |n\rangle$$

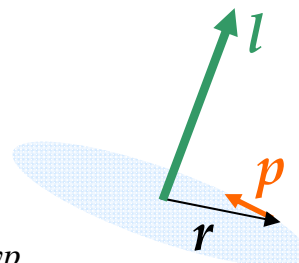
- The intensity of each line in an infra-red spectrum is governed by a transition dipole moment, which for a stretching vibration can be expressed as $q \langle n_2 | x | n_1 \rangle$. Here n_1 and n_2 are the vibrational quantum numbers before and after infra-red absorption, q is the difference in charge at each end of the bond, and x measures the displacement from the equilibrium bond length.

Adopting the simple harmonic oscillator model for the vibrations, x can be expressed in terms of raising and lowering operators, a and a^+ respectively, as $x = i(\hbar/2\mu\omega)^{1/2}(a - a^+)$ where μ is the reduced mass and ω the frequency of vibration. Using this relation, and the properties of a and a^+ , show how the usual infra-red selection rules, $\Delta n = n_2 - n_1 = \pm 1$, arise.

ANGULAR MOMENTUM IN QUANTUM MECHANICS

A particle moving with linear momentum \mathbf{p} (Cartesian components p_x, p_y, p_z) at a distance \mathbf{r} (x, y, z) from a given origin has an angular momentum about that point given by a vector cross-product expression;

$$\mathbf{l} = \mathbf{r} \times \mathbf{p} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = l_x \hat{i} + l_y \hat{j} + l_z \hat{k}$$



$$\text{Hence } l_x = yp_z - zp_y; \quad l_y = zp_x - xp_z; \quad l_z = xp_y - yp_x$$

This classical expression converts to quantum mechanical operator form through the usual transformation; p_x is replaced by the operator $-i\hbar \partial/\partial x$ for example. Thus we find;

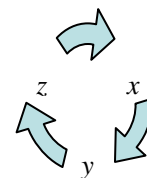
$$\hat{l}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right); \quad \hat{l}_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right); \quad \hat{l}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

Class exercise

Given the commutation result $[\hat{l}_x, \hat{l}_y] = i\hbar \hat{l}_z$, prove that $[\hat{l}^2, \hat{l}_z] = 0$.

Hint: Use cyclic permutations of the commutator, and the fact that $\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2$.

The physical consequence of latter result is that both the total angular momentum (squared) and its z-component can be simultaneously specified. This is why we can designate hydrogenic orbitals with both l and m quantum numbers, for example. It also proves very important in the interpretation of molecular rotation spectra – indeed there are temperature measuring devices based on the latter effect. But it is also noticeable that we cannot simultaneously specify two different angular momentum components – l_x and l_y for example – because the quantum operators do not commute



CHE-2H45 QUANTUM MECHANICS AND SYMMETRY

COURSEWORK PROBLEMS DUE MONDAY, WEEK 7

1. Explain what is meant by a *stationary state*. [20%]

2. Evaluate the following commutators:

$$\left[x^2, \frac{\partial}{\partial x} \right] \quad [15\%]$$

$$\left[e^{-ix} \frac{\partial^2}{\partial x^2}, e^{ix} + i \frac{\partial}{\partial x} \right] \quad [20\%]$$

3. Determine the results of each of the following operations of raising and lowering operators, a^+ and a respectively, on simple harmonic oscillator states $|n\rangle$;

$$a|n\rangle, \quad a^+|n\rangle, \quad aaa^+a^+|n\rangle. \quad [15\%]$$

Using and developing these results as appropriate, evaluate

$$\langle n|(a-a^+)^2|n\rangle. \quad [20\%]$$

Explain also why $\langle n|(a-a^+)^3|n\rangle$ must be zero. [10%]

D. L. Andrews
October 2009