Theoretical Foundation

2.1 The time-independent Schrödinger Equation

In Lecture Notes 1 we gave a qualitative description of the quantized energy levels of a particle. When a particle is moving with one of these energies it has a special stability and the particle is said to be in a "stationary state". Excited states are not as stable as the ground state, but they do have a nonzero lifetime; i.e. a particle in an excited energy level spends some time in that state before losing its energy and returning to the ground state. A "stationary state" is a state of the particle in which the experimentally measurable properties of the particle do not change in time during the lifetime of the state. Since the properties of a particle are intimately related to its state as will be seen later, we say that stationary states are independent of time (within the lifetime of the state).

We now turn to a theoretical description of the stationary states of a particle. Given a particular particle, our objective is to find all stationary states of this particle, and predict quantitatively all its properties when it is in any one of these states. The fundamental equation that describes properties of microscopic particles in their stationary states is the (time-independent) Schrödinger equation. When written in its most concise form it appears as:

$$\hat{H}\,\Psi = E\,\Psi \qquad\qquad \text{Schrödinger equation} \qquad\qquad\qquad \text{eq 2.1}$$

where $\hat{H}$ is called the Hamiltonian <u>operator</u> of the particle. Operators will be discussed below. Suffice it to say here that they are not scalars. In eq 2.1, $\hat{H}$ should always be considered as a known quantity. It will be seen later that for any given particle, or a system of many particles, there are simple rules to write down $\hat{H}$ explicitly. Of course, in order to devise a procedure for solving eq 2.1, we have to write it as explicitly as needed. The unknowns in the Schrödinger equation are the scalar quantities E and Ψ. The former is a <u>constant</u> representing the energy of the particle, and Ψ is a <u>function</u> of the coordinates of the particle. Note that the Hamiltonian has energy units. Ψ is called the wavefunction or "state function" of the particle. There are infinitely many solutions of the Schrödinger equation for E and Ψ. The set of energy values obtained by solving eq 2.1 constitute the allowed energies of the particle. Associated with each distinct E value there is one (in some cases more than one) corresponding Ψ.

As an example of an explicit Schrödinger equation, let us consider a particle of known mass m moving in one dimension (1D), say along the x-axis, under the influence of a known potential energy function $V(x)$. The symbol x denotes the position of the particle on the x-axis; it is an independent variable ranging between $-\infty$ and $+\infty$ ("full space" in 1D). Independent variables should always be considered as known quantities because whenever needed we are free to choose their values. The explicit Schrödinger equation for this particle is

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V(x)\,\Psi = E\,\Psi \qquad\qquad\qquad\qquad \text{eq 2.2a}$$

where $\hbar = \frac{h}{2\pi}$. This is a second order ordinary differential equation for finding the state function $\Psi(x)$ for a specified E (which is, however, unknown initially). It is known that the general solution of a second order ordinary differential equation contains two arbitrary constants, call them A and B. Together with E there are 3 unknown constants in the general solution. In real-life applications, the

general circumstances under which a particle is moving, same for all of its states, are always known. For example, the particle under study may actually be trapped between two rigid walls separated by a given distance *a*. This means that we know the particle can never get out of the trap, and this fact imposes a severe restriction on the possible values of *E* (to be seen below); i.e. the physically allowed energy values are discrete (quantized).

Eq 2.2a can be formally written as

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V \right) \Psi = E\,\Psi$$
                                                                                                 eq 2.2b

Comparison with eq 2.1 shows that the terms inside the parentheses in eq 2.2b make up the Hamiltonian operator, $\hat{H}$, of the particle in this example. It consists of two parts: the second term *V* is the potential energy of the particle, a scalar quantity. The first term, however, is not a scalar. It is a constant ($-\hbar^2/2m$) times the "second derivative operator", $\frac{d^2}{dx^2}$. An operator such as this one is not meaningful by itself; to gain a meaning, it must always be written together with a function on its right side: the expression, $\frac{d^2}{dx^2}\Psi \equiv \frac{d^2\Psi}{dx^2}$, is thus meaningful because it says "take the second derivative of the function Ψ". More will be said about operators later.

2.2 Normalization of Ψ

All physically allowed solutions of eq 2.2a have the following form

Ψ(*x*) = N *f*(*x*)   eq 2.3a

where *f*(*x*) is a function containing no unknowns, and N is an arbitrary constant; i.e. the only unknown in eq 2.3a is the factor N. For many applications it is convenient to assign a real number to N by using the requirement:

$$\int_{-\infty}^{\infty} \Psi^*(x)\Psi(x)dx = 1$$ Normalization condition (1D)   eq 2.3b

where Ψ^* is the complex conjugate of Ψ.[1] Substituting from eq 2.3a, one sees that

$$N = \pm \frac{1}{\sqrt{I}} \qquad \text{with } I = \int_{-\infty}^{\infty} f^*(x)f(x)dx$$ eq 2.3c

Thus by calculating the definite integral *I* (the result is always a positive number), one obtains the value of N. The sign of N is not physically significant; one usually takes the plus sign. The factor N in eq 2.3a is known as a "normalization constant". When its value is chosen according to eq 2.3c so that Ψ satisfies the normalization condition 2.3b, we say that Ψ is a "normalized function".

Since eq 2.2a is the Schrödinger equation for a particle that has only one degree of freedom, eqs 2.3a-c are appropriate for such a case. Consider now a particle moving in 3-dimensional (3D) space. It has 3 degrees of freedom, meaning that 3 independent variables are needed to locate it in 3D space.

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[1] A complex number *z* is defined by 2 real numbers *a* and *b,* and the complex number $i=\sqrt{-1}$, as *z=a + i b*. The "complex conjugate" of *z* is *z*=a − i b*. The product, $z^*z = a^2 + b^2$ is always a <u>positive</u> number for all choices of *a* and *b*. Thus $\Psi(x)\,\Psi^*(x)$ is a positive number for all *x* values. $\Psi^*(x)$ is obtained from $\Psi(x)$ by replacing *i* with *–i* in the explicit expression for $\Psi(x)$.

The type of variables used for this purpose may be either Cartesian (*x*, *y*, *z*) or spherical polar coordinates (r, θ, ϕ). The Hamiltonian operator in eq 2.1 is now a function of 3 variables, and as a consequence, the state function Ψ is also a function of the same 3 variables. Analogs of Eqs 2.3a-c for this case are written in the following notation

$\Psi = N f$ Normalization constant, N   eq 2.4a

$\int \Psi^* \Psi \, d\tau = 1$ Normalization condition (General)   eq 2.4b

$N = \pm \frac{1}{\sqrt{I}}$ with $I = \int f^* f \, d\tau$ eq 2.4c

The purpose of this notation is to express the main concepts as simply as possible by hiding some unnecessary details. Thus, in these expressions the symbols for the variables are not explicitly shown, and only one integration symbol is written in eqs 2.4a,b. Details are easily filled in when we actually perform the integration. For the particle in 3D, we know that there are 3 independent variables. The type of these variables is inferred from the explicit expression for Ψ which must be available in order to evaluate the integrals. The number of integrations to be done is equal to the number of variables; i.e. 3 in this case (triple integral). The symbol $d\tau$ is called "volume element". The expression for $d\tau$ depends on the type of variables used. If Cartesian variables are involved, $d\tau = dx\,dy\,dz$. On the other hand, for spherical polar variables, it is: $d\tau = r^2 \sin(\theta)\, dr\,d\theta\,d\phi$. Finally, limits of the definite integrals are "all space". In Cartesian variables, "all space" means: *x*, *y*, *z* each ranging from $-\infty$ to $+\infty$. In spherical polar variables "all space" is: *r* goes from 0 to ∞, θ ranges from 0 to π, and ϕ from 0 to 2π. Note the different ranges of the angle variables θ and ϕ.

With appropriate interpretation of the hidden "details" you may see that eqs 2.4a-c are perfectly general: they apply to all cases. For example, for a particle in 1D there is only one independent variable, call it *x*. There is only one integration to be done with $d\tau = dx$, and "all space" is *x* ranging from $-\infty$ to $+\infty$. Thus eqs 2.4a-c reduce to eqs 2.3a-c. In general, for a system of *n* particles moving in the 3D space, the number of independent variables is 3*n* (3 for each particle). The integrals are 3*n* dimensional. The volume element is a product: $d\tau = d\tau_1 d\tau_2 \dots d\tau_n$, where each single-particle volume element has the same expression (but with subscripts attached to the variables to distinguish between the particles) as the one discussed in the previous paragraph. Limits of the integrals are "all space" for each particle.

This approach of hiding "details" in order to emphasize "main ideas" is used throughout quantum chemistry. Otherwise, expressions would appear very complicated so that one would have a hard time in distinguishing details from fundamental concepts. For example, the compact form of the Schrödinger equation (eq 2.1) is perfectly general (it can be used for all cases) in this sense, and emphasizes the eigenvalue-eigenfunction concept (to be discussed). The "detail" here is the procedure for rewriting it when needed as an explicit equation suitable for applying mathematical methods to solve it; i.e. the rules for making $\hat{H}$ explicit. They will be discussed below. The explicit 1D Schrödinger equation (eq 2.2a) is a special case of eq 2.1.

Example 2.1 The ground state wavefunction of the electron in the hydrogen atom is ψ=C e^{-r/a_0} where C is a constant and $a_0 = 52.92 \, pm$ is the Bohr radius. Normalize ψ.

Procedure: The factor C is a normalization constant. To calculate its value from eq 2.4b,c we note that the electron is moving in 3D. Hence there are 3 independent variables, and *I* is a triple integral. The type of variables to use in the integrations is inferred from the expression for $f = e^{-r/a_0}$. The symbol *r* in *f* indicates the spherical polar variables. Thus, $d\tau = r^2 \sin(\theta)\, dr d\theta d\phi$, and

$$I = \int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\phi \; e^{-2r/a_0} r^2 \sin(\theta) = I_1 I_2 I_3$$

$$I_1 = \int_0^\infty dr\, e^{-2r/a_0} r^2 = \frac{a_0^3}{4}, \qquad I_2 = \int_0^\pi d\theta \sin(\theta) = 2, \qquad I_3 = \int_0^{2\pi} d\phi = 2\pi$$

$I = \pi a_0^3$, and the normalized function is: $\psi = \dfrac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$

<u>Note:</u> $\int_0^\infty e^{-bx} x^n dx = \dfrac{n!}{b^{n+1}}$　where *b* must be a positive number, and *n*=0 or a positive integer.

2.3 Probability and the state function Ψ

Probability concepts play an important role in quantum mechanics. Probability, Pr, of occurrence of an event is represented by real numbers between 0 and 1, with Pr=1 meaning 100% certainty that the event has occurred. Pr is dimensionless (i.e. no units). Let us consider the motion of a single particle. It is a fundamental postulate of quantum theory that if the function *Ψ* of a given energy level is known, one can calculate all other properties of the particle in such a state, using the relevant *Ψ*. One such property is the probability of finding the particle in a given "volume element" located at some specified point in space. The probability of finding the particle in such a tiny volume is given by

Pr = Ψ*Ψ $d\tau$ 　　　　　　　　　　Probability within $d\tau$ 　　　　　　　　　　　　eq 2.5

where Ψ is the <u>normalized</u> state function. You should interpret this expression in line with the discussion in section 2.2. For example, assume that the particle is constrained to move along the *x*-axis. Then it will have only one degree of freedom, and Pr can be written in a (slightly) more explicit form

Pr(*x*) = Ψ*(*x*)Ψ(*x*) dx 　　　　　　Probability within a small interval dx around a point x

Probability of finding the particle in a large interval between *x*=*a* and *x*=*b* where *b*>*a* is obtained by

Pr $= \int_a^b \Psi(x)^* \Psi(x)\, dx$ 　　　　　Probability within Δ*x*=*b-a*　　　　　　　　　　eq 2.6

Note that the probability of finding the particle in "all space" is 1 (as it should be) because Ψ is normalized (eq 2.3b).

Requirements for acceptability of Ψ. Probability interpretation via eqs 2.5-6 of the state function imposes several restrictions on Ψ. Only those Ψ functions are physically acceptable that satisfy the following conditions: i) Ψ must be everywhere finite; i.e. it must not become infinite at some point in

space. ii) Ψ must be a continuous function of its variables. iii) Ψ must be a single-valued function at all points in space.

Exercise 2.1 Consider the function, $f(x) = e^{-ikx}$, defined for all *x* ranging between $-\infty$ and $+\infty$. Here *k* is a constant. Show that *f* is physically acceptable only for real values of *k* (i.e. the imaginary part of *k* must be zero).

2.4 Operators

An "operator" is a mathematical operation that is applied to a function. It is conventional to use the symbol "^" to distinguish an operator from a scalar (a number) when using single letters to represent such objects. Thus, meanings of the symbols $\hat{A}$ and *A* are very different; the former is an operator while the latter is a scalar.

In general, when an operator is applied to a function, the result is a different function. For example, let $\hat{D} = d/dx$ be the operator that takes the first derivative of a function with respect to *x*. Then, for an arbitrary function *f(x)*, the meaning of $\hat{D}f$ is df/dx, and we write $\hat{D}f = df/dx$. As another example, if $\hat{x}$ is the operator that multiplies a function by x, we write $\hat{x}f(x) = xf(x)$. As in these examples, action of an operator to a function always gives a scalar result.

The operators of quantum mechanics are <u>linear</u>. A "linear operator" has the following properties:

$$\hat{A}(f_1 + f_2) = \hat{A}f_1 + \hat{A}f_2 \qquad\qquad \text{eq 2.7}$$

$$\hat{A}(cf) = c\hat{A}f \qquad\qquad \text{eq 2.8}$$

where *c* is a constant. There is an algebra of linear operators, and we can construct new operators from given ones; e.g. $\hat{A}_3 = \hat{A}_1 + \hat{A}_2$, or $\hat{A}_4 = \hat{A}_1\hat{A}_2$. Effect of such compound operators on functions are defined as:

$$(\hat{A}_1 + \hat{A}_2)f = \hat{A}_1 f + \hat{A}_2 f \qquad\qquad \text{eq 2.9}$$

$$\hat{A}_1\hat{A}_2 f = \hat{A}_1(\hat{A}_2 f) \qquad\qquad \text{eq 2.10}$$

As an example of eq 2.10, let us consider the results of applying the operators products (i) $\hat{x}\hat{D}$ and (ii) $\hat{D}\hat{x}$ to an arbitrary function $f(x)$:

(i) $\hat{x}\hat{D}f(x) = \hat{x}(\hat{D}f) = \hat{x}\dfrac{df}{dx} = x\dfrac{df(x)}{dx}$ eq 2.11

(ii) $\hat{D}\hat{x}f(x) = \hat{D}(\hat{x}f) = \hat{D}(xf) = \dfrac{d}{dx}(xf) = f(x) + x\dfrac{df(x)}{dx}$ eq 2.12

It is seen that the final results in (i) and (ii) are not the same. The difference between the two results is not zero, but

$$\hat{x}\hat{D}f(x) - \hat{D}\hat{x}f(x) = -f(x) \qquad\qquad \text{eq 2.13}$$

Thus the <u>order</u> of operators in an operator product is important. We say that the operators $\hat{x}$ and $\hat{D}$ do not <u>commute</u>. There are many other operator pairs in quantum mechanics that do not commute. For some operator pairs it may be that simplifications similar to eq 2.11-12 give identical results.

Then we say that those two operators commute. For example, an arbitrary operator $\hat{A}$ commutes with all of its powers, $\hat{A}^n$.

Introducing the identity operator $\hat{1}$ that multiplies a function by 1, eq 2.13 may be written as

$$\left(\hat{x}\hat{D} - \hat{D}\hat{x}\right)f(x) = -\hat{1}f(x)$$ eq 2.14

and we have the operator identity:

$$\hat{x}\hat{D} - \hat{D}\hat{x} = -\hat{1}$$ eq 2.15

For any two operators, the operator expression, $\hat{A}\hat{B} - \hat{B}\hat{A}$, is called the "commutator" of $\hat{A}$ and $\hat{B}$. Eq 2.15 shows that the commutator of $\hat{x}$ and $\hat{D}$ is not zero, i.e. these two operators do not commute. It is common practice to omit the operator symbol "^" from letters (or numbers) representing <u>multiplication</u> operators. For example, eq 2.15 is usually written as

$$x\hat{D} - \hat{D}x = -1$$ eq 2.16

We will follow this practice.

Exercise 2.2 Find the commutator of: a) z^3 and d/dz, b) z^3 and $\partial/\partial y$ (y and z are independent variables). In each of these two cases, state whether the operators commute or not.

2.5 Eigenvalue-Eigenfunction Equation

Suppose that the result of operating on some function f by an operator $\hat{A}$ is simply the initial function multiplied by a <u>special constant</u> k:

$$\hat{A}f = kf$$ Eigenvalue-eigenfunction equation for operator $\hat{A}$ eq 2.17

If you compare the graphs of the functions f and kf (e.g. take a function of one variable), you will convince yourself that the two graphs will look very similar, differing only in the scale of function values. For example, they become zero at the same values of their variables, and they attain their maxima and minima at the same points. Considering the fact that, in general, an operator transforms a given function into a very different function, a function f that satisfies eq 2.17 is a <u>very special</u> one. It turns out that for a given operator $\hat{A}$, there are many (in fact, infinitely many) functions (with different values of k) obeying eq 2.17. The set of these special functions is called "eigenfunctions" of the given operator $\hat{A}$ (i.e. there is <u>one</u> operator $\hat{A}$, but there are infinitely many different functions, each obeying eq 2.17 with a different value for k). Each eigenfunction is associated with a corresponding value of k via eq 2.17. The set of different k values is called "eigenvalues" of the operator $\hat{A}$. Eigenvalues of quantum mechanical operators are <u>real</u> numbers whereas there is no such restriction for the eigenfunctions; i.e. the latter may be complex-valued.

If an eigenfunction f in eq 2.17 is replaced by cf where c is an arbitrary constant, the latter function will also satisfy eq 2.17 with the same eigenvalue k due to the property given in eq 2.8.[2] This arbitrariness is removed by normalizing the eigenfunctions so that (see eq 2.4b):[3]

$$\int f^* f \, d\tau = 1 \qquad\qquad\qquad\qquad\qquad\qquad\text{eq 2.18}$$

In the light of the operator concept, and the eigenvalue-eigenfunction equation 2.17, we can better comprehend the Schrödinger equation, eq 2.1 (this is another example of main ideas vs. details). When we decide on studying the properties of a given system (e.g. a single particle, or an atom with many electrons, or a molecule, etc.), we always know the explicit expression for the Hamiltonian operator $\hat{H}$ of the system. $\hat{H}$ is a function of the variables needed to locate spatial positions of particles in the system. Thus, the Schrödinger equation is an eigenvalue-eigenfunction equation for $\hat{H}$. The allowed energies of the system are eigenvalues of $\hat{H}$, and the state functions are eigenfunctions of $\hat{H}$.

Orthogonality of eigenfunctions. Two different functions g and h of any number of variables are said to be "orthogonal" if the following definite integral involving them vanishes:

$$\int g^* h \, d\tau = 0 \qquad\qquad \text{Orthogonality} \qquad\qquad\qquad \text{eq 2.19}$$

Let k_1, k_2, … be the various eigenvalues of a given operator $\hat{A}$, arranged in increasing order. The corresponding eigenfunctions are denoted as f_1, f_2, … . It can be shown that any pair of functions selected from the set of eigenfunctions satisfies eq 2.19

$$\int f_n^* f_m \, d\tau = 0, \quad n \neq m \qquad\qquad \text{Orthogonality of eigenfunctions} \qquad\qquad \text{eq 2.20}$$

We say that the eigenfunctions of the operator $\hat{A}$ are <u>orthogonal</u>. If, in addition, the eigenfunctions are normalized (eq 2.18), they are called "orthonormal" (a word derived from the two words: <u>orthog</u>onal and <u>normal</u>ized).

Exercise 2.3 Consider the function, $g = c_1 f_1 + c_2 f_2$, where f_1 and f_2 are orthonormal functions. For g to be normalized, what must be the relation between the constants c_1 and c_2?

Commuting and noncommuting operators. It has been mentioned in section 2.4 that while, in general, two quantum mechanical operators do not commute, there are operator pairs that do commute. For example, an operator $\hat{A}$ always commutes with its powers, and any expression involving its powers. Thus, you should easily show that $\hat{A}$ commutes with itself, and also with $\hat{A}^2$, $\hat{A}^3$, …, or with an operator such as $\hat{B} = c_1\hat{A} + c_2\hat{A}^2 + c_3\hat{A}^3$ where c_1, c_2, and c_3 are given constants. Another important case is when the two operators depend on different <u>independent</u> variables. For example, operator pairs such as $\hat{D}_x = \partial/\partial x$ and $\hat{D}_y = \partial/\partial y$, (partial derivatives) always commute because x and y are independent variables. Another example is where $\hat{A}$ depends on spatial variables whereas $\hat{B}$ depends on "spin" (of an electron) variables. The latter type of variable (spin) will appear later in this course. The spin variables are independent of the space variables, and therefore any operator expression of spin variables always commutes with an operator of spatial variables.

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[2] In enumerating different eigenfunctions of eq 2.17, no distinction can be made between f and a multiple of it, $c\,f$. In quantum mechanics, f and $c\,f$ are always regarded as the "same" eigenfunction.
[3] See section 2.2 for how to fill in "details" in the integrals of eqs 2.18-20.

The significance of <u>commuting operators</u> is that when two or more operators commute, they have the <u>same</u> set of eigenfunctions.

Exercise 2.4 Show that if f is an eigenfunction of $\hat{A}$ with eigenvalue k, (eq 2.17), then the same function f is also an eigenfunction of the operator $\hat{B}=c_1\hat{A}+c_2\hat{A}^2+c_3\hat{A}^3$ with eigenvalue $b=c_1k+c_2k^2+c_3k^3$.

2.6 Rules for writing explicit expressions for quantum mechanical operators

Experimentally measurable properties of a system are called its "observables". Quantum theory associates each observable with a linear operator. Expressions for the operators are obtained from known classical mechanical expressions for the observables, using simple rules. All classical quantities must be expressed using Cartesian variables for the positions of particles, and their linear momenta. The classical expression for the potential energy function, V, is used in quantum theory without any modification. In all quantum chemical applications, V is a function of coordinates only.

We will use the standard symbol T for the classical kinetic energy. Let us consider a particle of mass m, moving in 3D. T must be written in terms of the linear momentum, $\vec{p}$, of the particle before converting T into a quantum operator. Linear momentum is a vector with Cartesian components: $\vec{p} = (p_x, p_y, p_z)$. The classical kinetic energy of the particle is given by

$$\text{T} = \frac{p^2}{2m} \quad \text{where } p^2 = p_x^2 + p_y^2 + p_z^2 \qquad \qquad \text{eq 2.21}$$

In classical mechanics, the sum of the kinetic energy (expressed in terms of momenta) and the potential energy of a material system is known as the hamiltonian of the system, denoted by the standard symbol H; i.e. H=T+V. Classical H is a constant, equal to the total energy of the system: H=E. For our single particle example, it is:

$$\text{H} = \frac{p^2}{2m} + \text{V}(x, y, z) \qquad \qquad \text{eq 2.22}$$

Expressions for quantum operators are obtained from their classical counterparts by the following rule: each Cartesian component of linear momentum p_q in the classical expression is replaced by the operator

$$\hat{p}_q = -i\,\hbar\,\frac{\partial}{\partial q}, \qquad q = x, y, z \qquad \qquad \text{eq 2.23}$$

where $i = \sqrt{-1}$ and $\hbar = h/2\pi$ are constants, and (*x,y,z*) are the Cartesian coordinates of the particle. The operator for p_q^2 is obtained by using eq 2.10

$$\hat{p}_q^2 = -\hbar^2\,\frac{\partial^2}{\partial q^2}, \qquad q = x, y, z \qquad \qquad \text{eq 2.24}$$

The kinetic energy operator for a single particle in 3D space is thus

$$\hat{T} = \frac{\hat{p}^2}{2m} = \frac{1}{2m}\left(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2\right) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \qquad \text{eq 2.25}$$

and the explicit Hamiltonian operator is

$$\hat{H} = \hat{T} + V = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x,y,z) \qquad\qquad \text{eq 2.26}$$

Exercise 2.5 Show that the functions $f_k = e^{-ikx}$ are eigenfunctions of $\hat{p}_x$. What are the eigenvalues? State the full range of numerical values for the eigenvalues. *Hint*: see Exercise 2.1 What is the unit of k?

Hamiltonian operator for a system of *n* particles. In chemistry, we study properties of atoms and molecules that contain many particles (electrons and nuclei). Let *n* be the number of particles in a given atom or a molecule. All of these particles are moving in the 3D space, and therefore, there are 3*n* independent position variables. Let us label the particles by the integers j=1,2, …,*n* such that the j$^{\text{th}}$ particle has mass m_j, Cartesian position variables (x_j,y_j,z_j), and linear momentum vectors $\vec{p}_j = (p_{x_j}, p_{y_j}, p_{z_j})$. Classically, the total kinetic energy T of *n* particles is a sum of independent contributions from each particle

T=T_1+T_2+ … +T_n $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ eq 2.27

where $T_j = \frac{p_j^2}{2m_j}$ is the kinetic energy of the j$^{\text{th}}$ particle.

The corresponding quantum mechanical operator is

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_n \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{eq 2.28}$$

where each $\hat{T}_j$ has the same form as in eq 2.25 in which the mass *m* is replaced by m_j, and the coordinates (*x,y,z*) are replaced by (x_j,y_j,z_j), to indicate the j$^{\text{th}}$ particle. Note the mathematical structure of $\hat{T}$: it is a sum of terms such that each term $\hat{T}_j$ depends on the coordinates of only one particle. Many-particle operators that have this property are called "one-particle" operators. The Hamiltonian operator is obtained by adding the potential energy function of the system

$$\hat{H} = \hat{T} + V \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{eq 2.29}$$

2.7 Experimental measurements and theoretical calculations

Let A be one of the observables of the system under investigation, and let $\hat{A}$ be the associated quantum operator. $\hat{A}$ has infinitely many different eigenvalues {k_1, k_2, …} and corresponding eigenfunctions { $f_1, f_2,$ …} such that $\hat{A}f_n = k_n f_n$, for *n*=1, 2, 3, … It is a fundamental postulate of quantum theory that the only possible values that can result from measurements of property A are the eigenvalues {k_1, k_2, …} of the operator $\hat{A}$. A single measurement will give one of these eigenvalues. In repeated measurements, there might be dispersion in the results. The "average value" of the measurements is denoted by the symbol <A>, a standard notation in quantum mechanics. A synonymous term for <A> is the "expectation value" of observable A. According to quantum theory, this quantity which depends on the state of the system can be calculated by the following expression:

<A>= $\int \Psi^* \hat{A}\Psi \, d\tau$ $\qquad$ Expectation value of observable A $\qquad\qquad\qquad$ eq 2.30

where Ψ is a given <u>normalized</u> wavefunction for the state of interest (i.e. an allowed solution of the Schrödinger equation 2.1). Evaluation of the integral in eq 2.30 proceeds in two steps: i) one first simplifies the part $\hat{A}\Psi$ as much as possible by using the given (i.e. known) expressions for the operator $\hat{A}$ and the state function Ψ; ii) the resultant expression (i.e. a function) from the first step is multiplied by Ψ^*, and then the integral is evaluated.

It should be noted that unless $\hat{A}$ commutes with the Hamiltonian $\hat{H}$, the state function Ψ can <u>not</u> be an eigenfunction of $\hat{A}$, and as a consequence, $\hat{A}\Psi$ will be a different function than Ψ. In the special, but important case when $\hat{A}$ commutes with $\hat{H}$, Ψ will be proportional to one of the eigenfunctions f_n of $\hat{A}$ with eigenvalue k_n, which leads to the conclusion that $\hat{A}\Psi = k_n\Psi$.[4] In this case, the integral in eq 2.30 can be evaluated immediately

$$<A> = \int \Psi^* \hat{A}\Psi \, d\tau = k_n \int \Psi^* \Psi \, d\tau = k_n \qquad \text{eq 2.31}$$

because Ψ is normalized. Thus repeated measurements of property A will all result with the same value, k_n, (i.e. no dispersion) when the associated operator $\hat{A}$ commutes with the Hamiltonian operator of the system. An example is the measurement of the energy, E, of the system in a given stationary state. Since Ψ is one of the eigenfunctions of $\hat{H}$, say with eigenvalue E_n, every measurement of E of the system in this state will yield the same energy E_n. The usual notation for the average energy is <H>, rather than <E>.

Example 2.2 Calculate the average distance of the electron from the nucleus in H-atom for the ground state of the electron (see Example 2.1 for the normalized ground state Ψ).

Procedure: The observable is the <u>distance</u> of the electron from the nucleus. This is identified as the variable r in polar coordinates. Its average value is designated as <r>. The associated operator is $\hat{r}$; it multiplies any function with r: $\hat{r}\Psi = r\Psi$. The rest is a matter of evaluating a simple triple integral, and can be done in a similar way to that in Example 2.1. You will obtain, <r>=$3a_0$/2=79.4 pm.

2.8 Expansion of Ψ into a Linear Combination of Eigenfunctions

Suppose that Ψ for a given state of the system is available as an explicit expression. For some purposes in quantum theory, we wish to express it in the following special form

$$\Psi = c_1 f_1 + c_2 f_2 + c_3 f_3 + \cdots \qquad \text{eq 2.32}$$

where $\{f_1, f_2, \dots\}$ are normalized eigenfunctions of an operator $\hat{A}$, and $\{c_1, c_2, \dots\}$ are constants. It will be assumed that explicit expressions for all of the eigenfunctions are given. The sum on the right side is called "linear combination" of the functions $\{f_1, f_2, \dots\}$, and we say that we have "expanded" Ψ into a linear combination of these functions. For the expression 2.32 is to be useful, we must know how to calculate the coefficients from the given information. The orthogonality property (eq 2.20) of the eigenfunctions makes this task easy. In order to use it, we multiply both sides of eq 2.32 by the complex conjugate of one of the eigenfunctions f_n^*, and integrate

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[4] See the part "commuting and noncommuting operators" in section 2.5.

$$\int f_n^* \Psi \, d\tau = c_1 \int f_n^* f_1 d\tau + c_2 \int f_n^* f_2 d\tau + \cdots \qquad \text{eq 2.33}$$

Among the many integrals on the right side, due to the orthogonality property of the eigenfunctions, only one integral will be nonzero: the one with the nth coefficient c_n. The nonzero integral, $\int f_n^* f_n d\tau = 1$ because we are told that the eigenfunctions are normalized. Therefore, we can write

$$c_n = \int f_n^* \Psi \, d\tau \qquad \text{eq 2.34}$$

Since by hypothesis the explicit expressions for both f_n and Ψ are available, this definite integral can be evaluated for n=1, 2, …, in succession, yielding numerical values of all coefficients in eq 2.32.[5]

Probability interpretation of Ψ (eq 2.5-2.6) is valid only if it is normalized: $\int \Psi^* \Psi \, d\tau = 1$. We may express the normalization condition in terms of the coefficients in eq 2.32 as follows. We replace Ψ^* in the normalization integral by its expansion (eq 2.32), and use eq 2.34:[6]

$$\int (c_1^* f_1^* + c_2^* f_2^* + \cdots) \Psi \, d\tau = c_1^* \int f_1^* \Psi \, d\tau + c_2^* \int f_2^* \Psi \, d\tau + \cdots = |c_1|^2 + |c_2|^2 + \cdots = 1$$

Thus

$$\sum |c_n|^2 = 1 \qquad \text{eq 2.35}$$

when Ψ in eq 2.32 is normalized.

It is of interest to express the average value of observable A (eq 2.30) in the given state in terms of these coefficients since it leads to a theoretical prediction of the probability of observing each eigenvalue k_n of the operator $\hat{A}$. We first simplify the term $\hat{A}\Psi$ in the integrand of eq 2.30 where Ψ has the form in eq 2.32.

$$\hat{A}\Psi = \hat{A}(c_1 f_1 + c_2 f_2 + c_3 f_3 + \cdots) = c_1 k_1 f_1 + c_2 k_2 f_2 + c_3 k_3 f_3 + \cdots$$

Then

$$\int \Psi^* (c_1 k_1 f_1 + c_2 k_2 f_2 + c_3 k_3 f_3 + \cdots) d\tau = c_1 k_1 \int \Psi^* f_1 d\tau + c_2 k_2 \int \Psi^* f_2 d\tau + \cdots$$

Comparison with eq 2.34 shows that the value of each integral on the right side is simply c_n*. Thus we obtain the desired expression:

$$<A> = \int \Psi^* \hat{A}\Psi \, d\tau = k_1 |c_1|^2 + k_2 |c_2|^2 + \cdots \qquad \text{eq 2.36}$$

If $\hat{A}$ does not commute with $\hat{H}$, many of the coefficients calculated by eq 2.34 will not be zero. In this case, the average value of observable A in the state Ψ is a weighted average of eigenvalues of the associated operator $\hat{A}$. The weight factor $|c_n|^2$ of each eigenvalue k_n is interpreted as the probability of getting k_n in a measurement of property A. As seen from eq 2.35, the sum of all probabilities is 1, in agreement with the probability concept. On the other hand, if $\hat{A}$ commutes with $\hat{H}$ then Ψ must be one of the eigenfunctions {f_1, f_2, …} of $\hat{A}$, e.g. f_n for a given n, and because of the orthogonality

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[5] If the eigenfunctions and/or Ψ are complex-valued functions, values of the coefficients may be complex numbers.
[6] For any two complex numbers z_1 and z_2, one has the identities: $(z_1+z_2)^*=z_1^*+z_2^*$ and $(z_1 z_2)^*=z_1^* z_2^*$

property, eq 2.35 will give a nonzero result for only one coefficient: c_n=1. This case has been discussed previously (eq 2.31).

Exercise 2.6 Given

$$\hat{A}f_m = \hbar m f_m, \qquad m = 0, \pm 1, \pm 2 \dots$$

Assume that the particle is in a state with $\Psi = C\ (f_0 - 2f_1 + 3f_{-2})$, where C is a constant. The functions f_m are normalized. In measurements of property A of the particle in this state, what are the possible outcomes for A, and the probability of each outcome?

Additional Exercises for this part:

Problems 16, 17, 18, 21, 26 in Chapter 11 of Physical Chemistry (4th ed.) by Laidler, Meiser and Sanctuary