The sp³ Hybrid Orbitals in NH₃ and H₂O
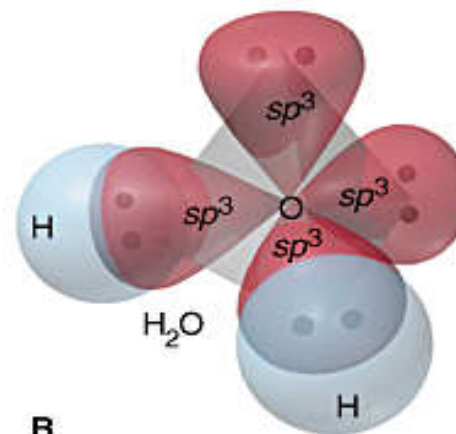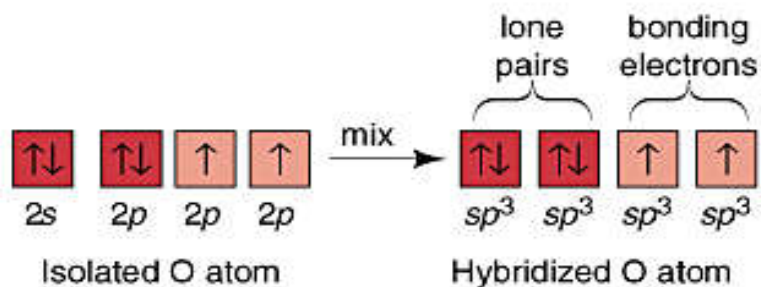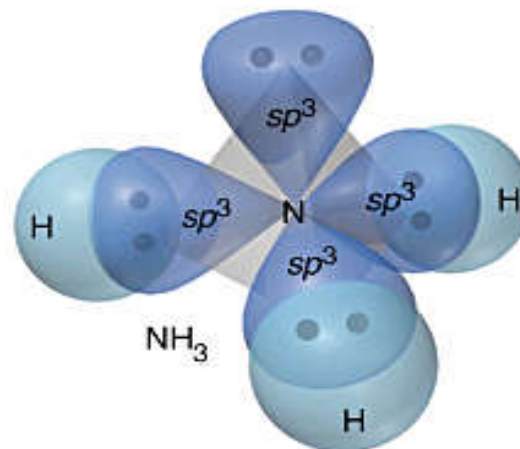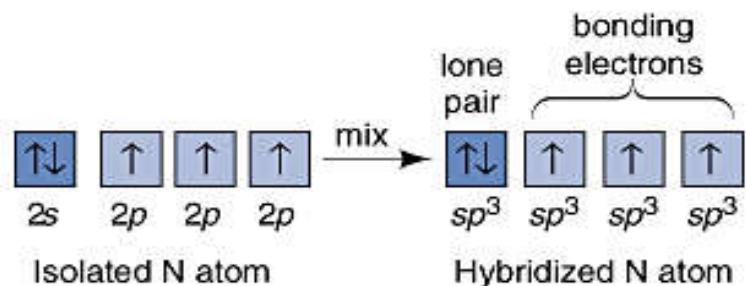
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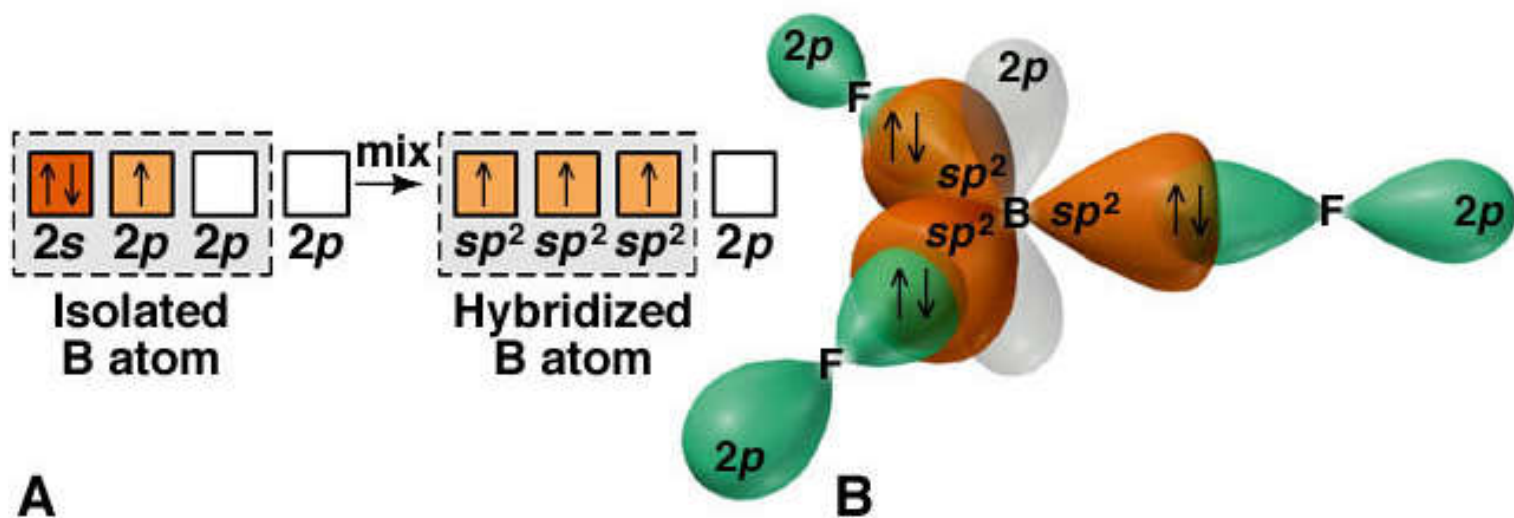
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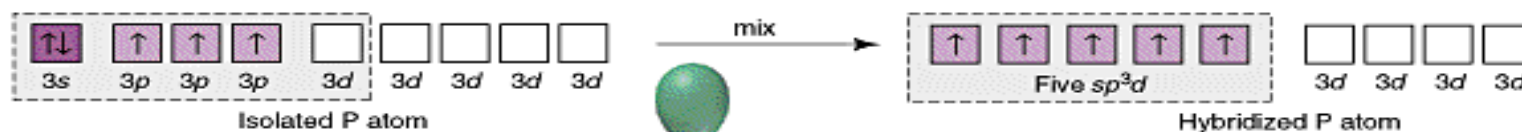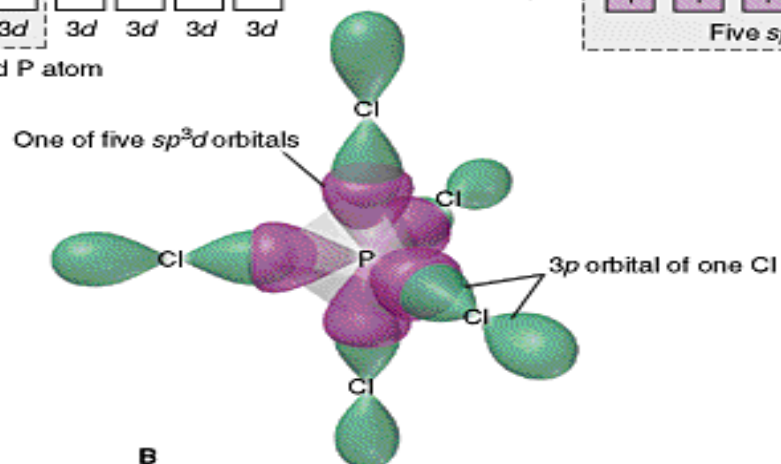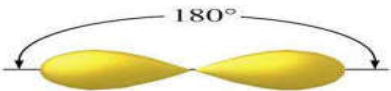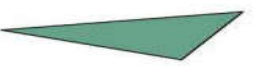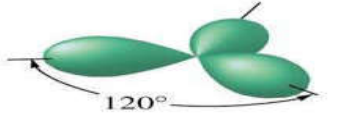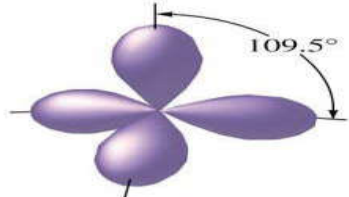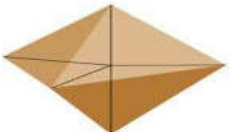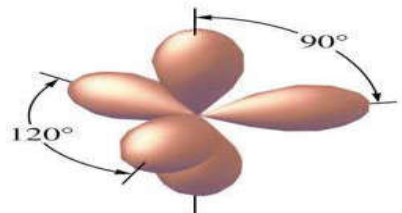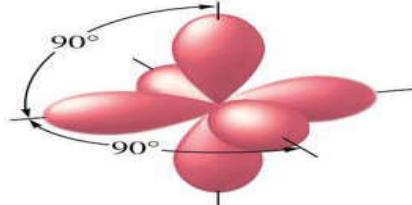
The sp³d² Hybrid Orbitals in SF₆
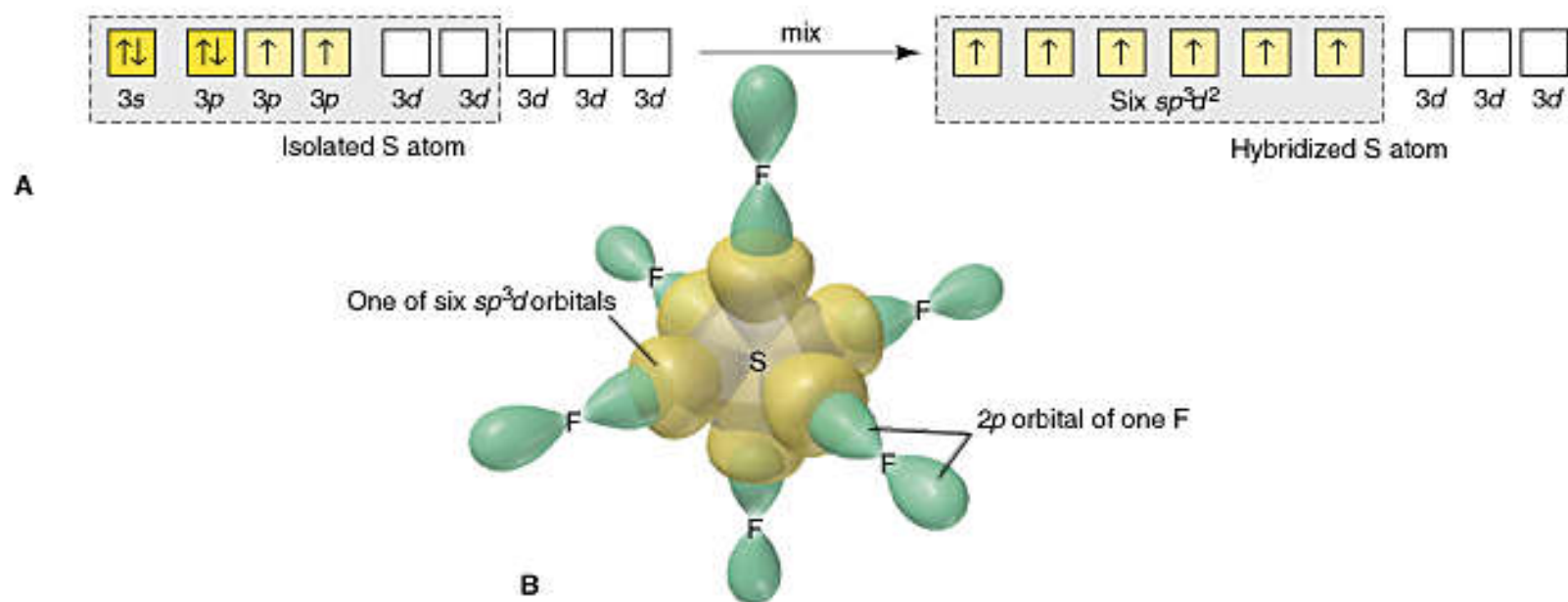
Number of Effective Pairs	Arrangement of Pairs			Hybridization Required
2		Linear	sp	180°
3		Trigonal planar	sp^2	120°
4		Tetrahedral	sp^3	109.5°
5		Trigonal bipyramidal	dsp^3	90° 120°
6		Octahedral	d^2sp^3	90° 90°

Molecular Orbital Theory:

Node

π Antibonding MO
(unfilled)

π Bonding MO
(filled)

Two *p* orbitals

Combine

Energy
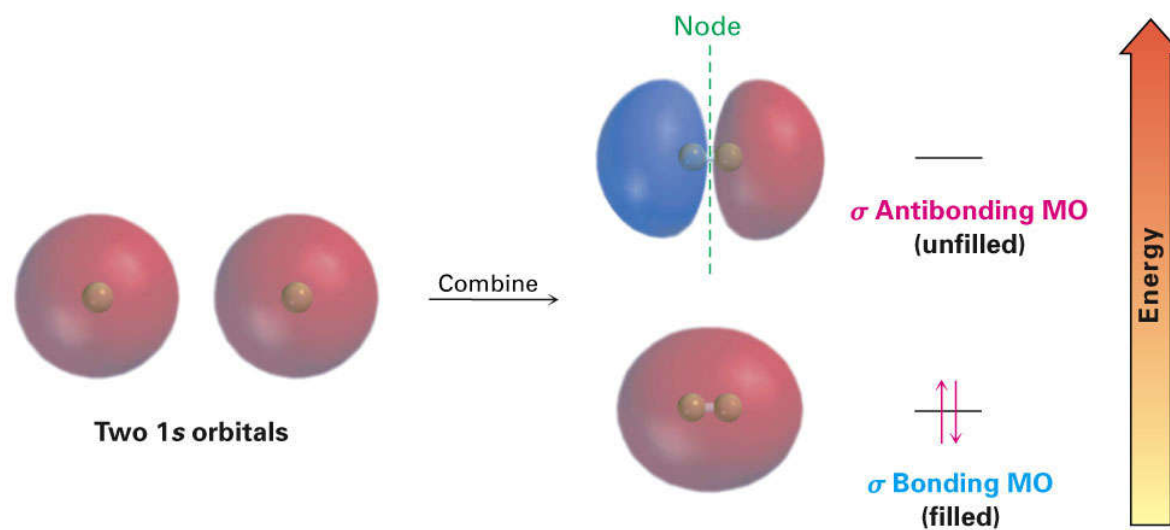
© 2007 Thomson Higher Education

117
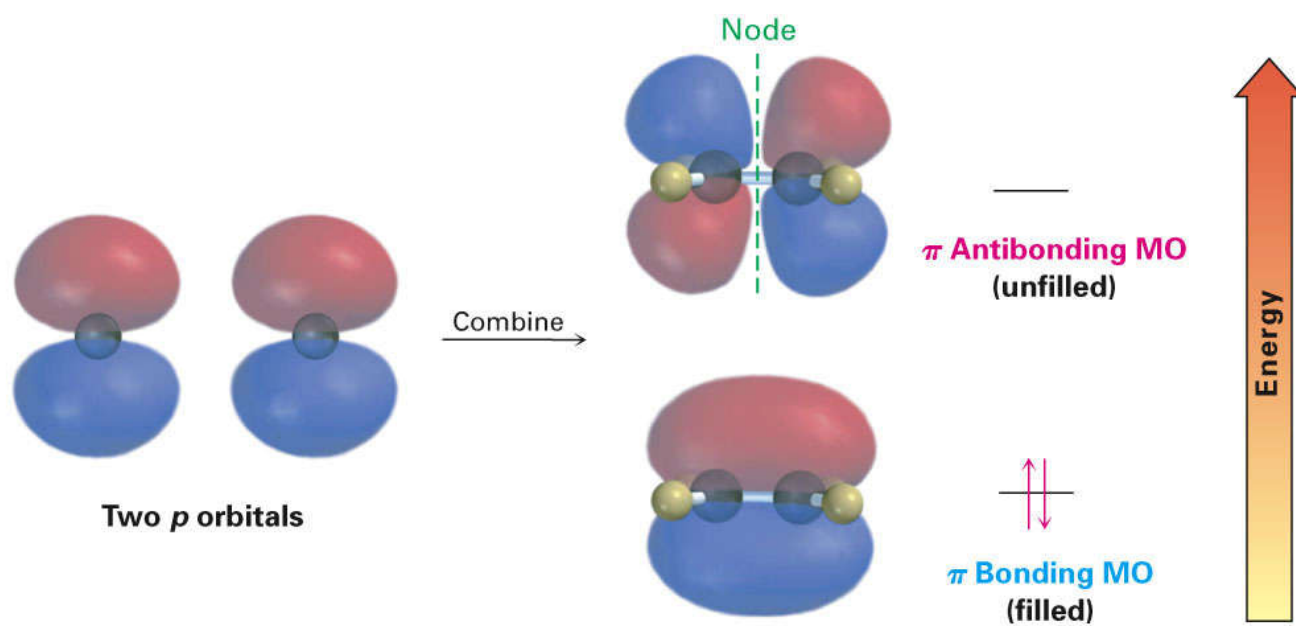
Formation of Sigma Molecular Orbitals:

1. Overlapping of two 1s atomic orbital

Example: H_2

bonding

antibonding
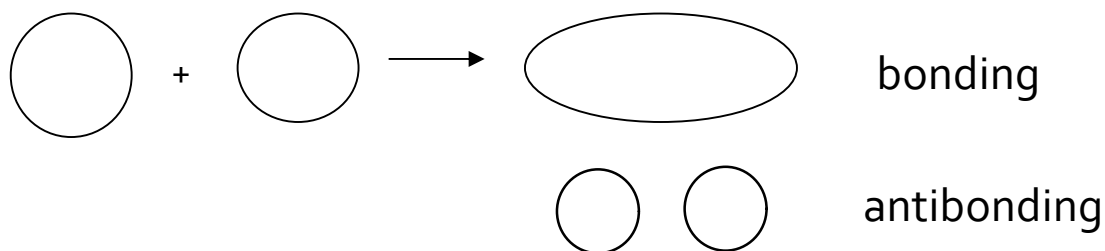
2. Overlapping of two px atomic orbital

bonding

antibonding

118
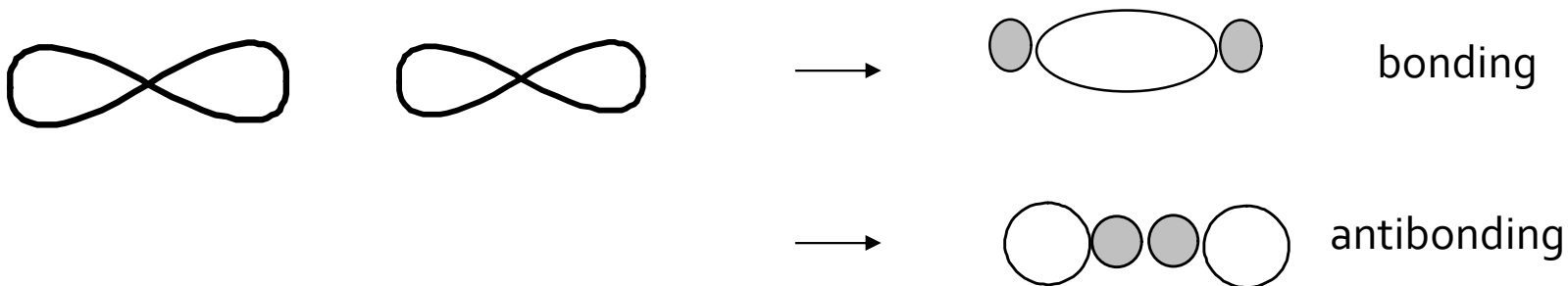
3. Overlapping of an s and px atomic orbitals

bonding

antibonding
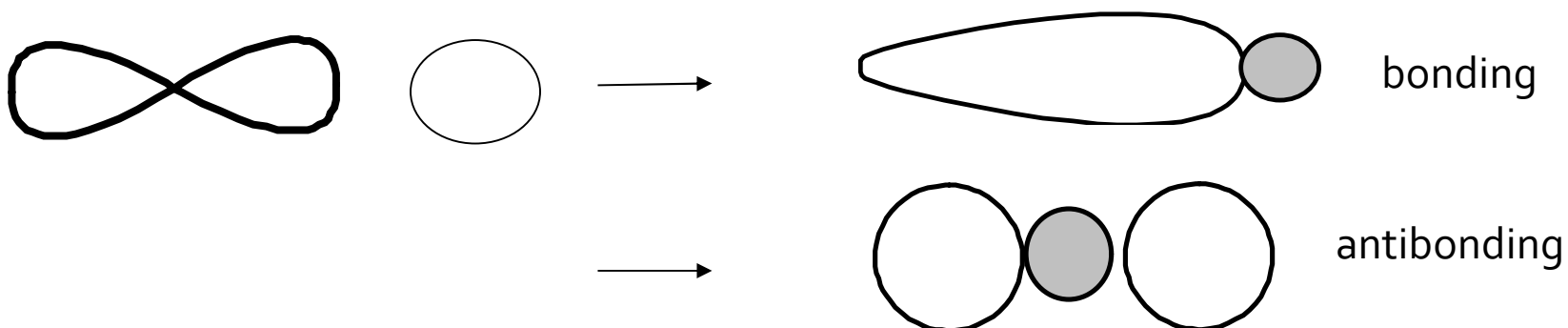
4. Overlapping of px and dz^2 or dx^2-y^2

bonding

antibonding
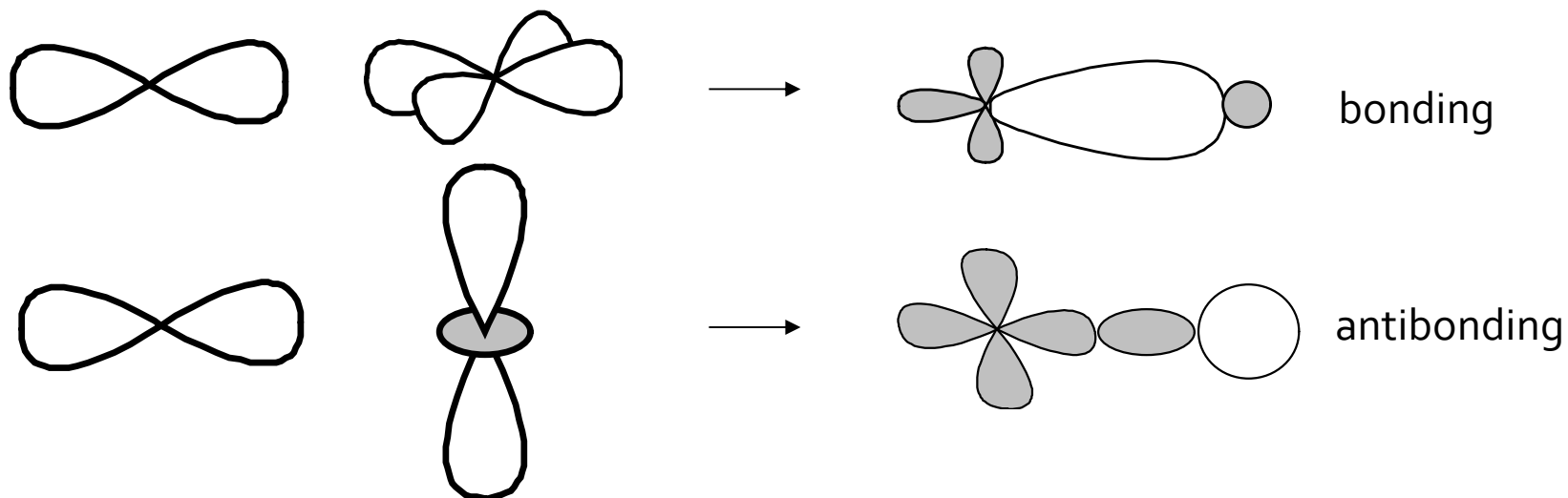
Computational chemistry:

Computational chemistry uses result of theoretical chemistry incorporated into efficient computer programmed to calculate structure and properties of molecule.

It calculate the properties of molecule such as structure, relative energy, charge distribution, dipole moment, vibrational frequency, reactivity and other spectroscopic quantity.

- **Classical Methods:**

1. Molecular Mechanics.

2. Molecular Dynamics.

- **Quantum Mechanics Methods:**

1. Semi empirical Methods.

2. Ab initio Methods.

3. Density functional Theory.

The Time-Dependent Schrödinger Equation:

Classical mechanics applies only to macroscopic particles. For microscopic "particles" we require a new form of mechanics, called quantum mechanics. We now consider some of the contrasts between classical and quantum mechanics. For simplicity a one-particle, one-dimensional system will be discussed.

In classical mechanics the motion of a particle is governed by Newton's second law:

$$F = ma = m\frac{d^2x}{dt^2} \qquad (1.8)$$

where F is the force acting on the particle, m is its mass, and t is the time; a is the acceleration, given by a = dv/dt = (d/dt)(dx/dt) = (d^2x/dt^2), where v is the velocity. Equation (1.8) contains the second derivative of the coordinate x with respect to time. To solve it, we must carry out two integrations. This introduces two arbitrary constants c_1 and c_2 into the solution, and

$$x = g(t, c_1, c_2) \qquad (1.9)$$

where g is some function of time. We now ask: What information must we possess at a given time t_0 to be able to predict the future motion of the particle? If we know that at t_0 the particle is at point x_0, we have:

$$x_0 = g(t_0, c_1, c_2) \qquad (1.10)$$

Since we have two constants to determine, more information is needed. Differentiating (1.9), we have

$$\frac{dx}{dt} = v = \frac{d}{dt} g(t, c_1, c_2)$$

If we also know that at time t_0 the particle has velocity v_0, then we have the additional relation

$$v_0 = \frac{d}{dt} g(t, c_1, c_2) \Big|_{t=t_0} \qquad (1.11)$$

We may then use (1.10) and (1.11) to solve for c_1 and c_2 in terms of x_0 and v_0. Knowing c_1 and c_2, we can use Eq. (1.9) to predict the exact future motion of the particle.

As an example of Eqs. (1.8) to (1.11), consider the vertical motion of a particle in the earth's gravitational field. Let the x axis point upward. The force on the particle is downward and is $F = -mg$, where g is the gravitational acceleration constant. Newton's second law (1.8) is:

$$-mg = m\,d^2x/dt^2, \text{ so } d^2x/dt^2 = -g$$

A single integration gives $dx/dt = -gt + c_1$. The arbitrary constant c_1 can be found if we know that at time t_0 the particle had velocity v_0. Since $v = dx/dt$, we have $v_0 = -gt_0 + c_1$ and $c_1 = v_0 + gt_0$.

Therefore, $dx/dt = -gt + gt_0 + v_0$. Integrating a second time, we introduce another arbitrary constant c_2, which can be evaluated if we know that at time t_0 the particle had position x_0.

$$x = x_0 - \frac{1}{2} g (t - t_0)^2 + v_0 (t - t_0)$$

Knowing x_0 and v_0 at time t_0, we can predict the future position of the particle.

The classical-mechanical potential energy V of a particle moving in one dimension is defined to satisfy:

$$\frac{\partial V(x,\, t)}{\partial x} = -F(x,\, t) \qquad\qquad (1.12)$$

For example, for a particle moving in the earth's gravitational field, $\partial V/\partial x$ = -F = mg and integration gives V = mgx + c, where c is an arbitrary constant. We are free to set the zero level of potential energy wherever we please. Choosing c = 0, we have V = mgx as the potential-energy function.

To describe the state of a system in quantum mechanics, we postulate the existence of a function Ψ of the particles' coordinates called the state function or wave function (often written as wavefunction). Since the state will, in general, change with time, Ψ is also a function of time. For a one-particle, one-dimensional system, we have:

$$\Psi = \Psi(x, t)$$

For a one-particle, one-dimensional system, this equation is postulated to be:

$$-\frac{\hbar}{i}\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) \qquad (1.13)$$

where the constant $\hbar$ (**h-bar**) is defined as

$$\hbar \equiv \frac{h}{2\pi} \qquad (1.14)$$

The concept of the wave function and the equation governing its change with time were discovered in 1926 by the Austrian physicist Erwin Schrödinger (1887–1961). In this equation, known as the time-dependent Schrödinger equation (or the Schrödinger wave equation):

$i = \sqrt{-1}$, m is the mass of the particle, and

$V(x, t)$ is the potential-energy function of the system.

We begin by restricting ourselves to the special case where the potential energy V is not a function of time but depends only on x. This will be true if the system experiences no time-dependent external forces. The time-dependent Schrödinger equation reads:

$$-\frac{\hbar}{i}\frac{\partial \Psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x)\Psi(x, t) \tag{1.16}$$

We now restrict ourselves to looking for those solutions of (1.16) that can be written as the product of a function of time and a function of x:

$$\Psi(x, t) = f(t)\psi(x) \qquad\qquad (1.17)$$

Capital psi is used for the time-dependent wave function and lowercase psi for the factor that depends only on the coordinate x.

Taking partial derivatives of (1.17), we have:

$$\frac{\partial \Psi(x, t)}{\partial t} = \frac{df(t)}{dt}\psi(x), \qquad \frac{\partial^2 \Psi(x, t)}{\partial x^2} = f(t)\frac{d^2\psi(x)}{dx^2}$$

Substitution into (1.16) gives:

$$-\frac{\hbar}{i}\frac{df(t)}{dt}\psi(x) = -\frac{\hbar^2}{2m}f(t)\frac{d^2\psi(x)}{dx^2} + V(x)f(t)\psi(x)$$

$$-\frac{\hbar}{i}\frac{1}{f(t)}\frac{df(t)}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + V(x) \qquad (1.18)$$

Equating the left side of (1.18) to E, we get:

$$\frac{df(t)}{f(t)} = -\frac{iE}{\hbar} dt$$

Integrating both sides of this equation with respect to t, we have:

$$\ln f(t) = -iEt/\hbar + C$$

where C is an arbitrary constant of integration. Hence:

$$f(t) = e^C e^{-iEt/\hbar} = Ae^{-iEt/\hbar}$$

where the arbitrary constant A has replaced e^C. Since A can be included as a factor in the function $\psi(x)$ that multiplies $f(t)$ in (1.17), A can be omitted from $f(t)$. Thus:

$$f(t) = e^{-iEt/\hbar}$$

Equating the right side of (1.18) to E, we have:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \qquad (1.19)$$

Equation (1.19) is the time-independent Schrödinger equation for a single particle of mass m moving in one dimension.

What is the significance of the constant E? Since E occurs as [E – V(x)] in (1.19), E has the same dimensions as V, so E has the dimensions of energy. In fact, we postulate that E is the energy of the system. Thus, for cases where the potential energy is a function of x only, there exist wave functions of the form:

$$\Psi(x, t) = e^{-iEt/\hbar}\psi(x) \tag{1.20}$$

and these wave functions correspond to states of constant energy E.

Operators:

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \right]\psi(x) = E\psi(x) \qquad (3.1)$$

The entity in brackets in (3.1) is an operator. Equation (3.1) suggests that we have an energy operator, which, operating on the wave function, gives us the wave function back again, but multiplied by an allowed value of the energy.

If $\hat{3}$ is the operator that multiplies a function by 3, then:

$$\hat{3}(x^2 + 3e^x) = 3x^2 + 9e^x$$

$\hat{A}$ transforms the function f(x) into the function g(x), we write $\hat{A}$ f(x) = g(x).

We define the sum and the difference of two operators $\hat{A}$ and $\hat{B}$ by

$$(\hat{A} + \hat{B})f(x) \equiv \hat{A}f(x) + \hat{B}f(x) \qquad \text{(3.2)}$$

$$(\hat{A} - \hat{B})f(x) \equiv \hat{A}f(x) - \hat{B}f(x)$$

The product of two operators $\hat{A}$ and $\hat{B}$ is defined by:

$$\hat{A}\hat{B}f(x) \equiv \hat{A}\left[\hat{B}f(x)\right]$$

(3.3)

In other words, we first operate on f(x) with the operator on the right of the operator product, and then we take the resulting function and operate on it with the operator on the left of the operator product.

Operators obey the associative law of multiplication:

$$\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C} \tag{3.6}$$

The proof of (3.6) is outlined in Prob. 3.10. As an example, let $\hat{A} = d/dx$, $\hat{B} = \hat{x}$, and $\hat{C} = 3$. Using (3.5), we have

$$(\hat{A}\hat{B}) = \hat{D}\hat{x} = 1 + \hat{x}\hat{D}, \qquad [(\hat{A}\hat{B})\hat{C}]f = (1 + \hat{x}\hat{D})3f = 3f + 3xf'$$

$$(\hat{B}\hat{C}) = 3\hat{x}, \qquad [\hat{A}(\hat{B}\hat{C})]f = \hat{D}(3xf) = 3f + 3xf'$$

A major difference between operator algebra and ordinary algebra is that numbers obey the commutative law of multiplication, but operators do not necessarily do so; $ab = ba$ if a and b are numbers, but $\hat{A}\hat{B}$ and $\hat{B}\hat{A}$ are not necessarily equal operators. We define the **commutator** $[\hat{A}, \hat{B}]$ of the operators $\hat{A}$ and $\hat{B}$ as the operator $\hat{A}\hat{B} - \hat{B}\hat{A}$:

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \tag{3.7}$$

If $\hat{A}\hat{B} = \hat{B}\hat{A}$, then $[\hat{A}, \hat{B}] = 0$, and we say that $\hat{A}$ and $\hat{B}$ **commute**. If $\hat{A}\hat{B} \neq \hat{B}\hat{A}$, then $\hat{A}$ and $\hat{B}$ do not commute. Note that $[\hat{A}, \hat{B}]f = \hat{A}\hat{B}f - \hat{B}\hat{A}f$. Since the order in which we apply the operators 3 and d/dx makes no difference, we have

$$\left[\hat{3}, \frac{d}{dx}\right] = \hat{3}\frac{d}{dx} - \frac{d}{dx}\hat{3} = 0$$

From Eq. (3.5) we have

$$\left[\frac{d}{dx}, \hat{x}\right] = \hat{D}\hat{x} - \hat{x}\hat{D} = 1 \tag{3.8}$$

The operators d/dx and $\hat{x}$ do not commute.

The **square** of an operator is defined as the product of the operator with itself: $\hat{B}^2 = \hat{B}\hat{B}$. Let us find the square of the differentiation operator:

$$\hat{D}^2 f(x) = \hat{D}(\hat{D}f) = \hat{D}f' = f''$$

$$\hat{D}^2 = d^2/dx^2$$

As another example, the square of the operator that takes the complex conjugate of a function is equal to the unit operator, since taking the complex conjugate twice gives the original function. The operator $\hat{B}^n$ ($n = 1, 2, 3, \ldots$) is defined to mean applying the operator $\hat{B}$ n times in succession.

It turns out that the operators occurring in quantum mechanics are linear. $\hat{A}$ is a **linear operator** if and only if it has the following two properties:

$$\hat{A}[f(x) + g(x)] = \hat{A}f(x) + \hat{A}g(x) \tag{3.9}$$

$$\hat{A}[cf(x)] = c\hat{A}f(x) \tag{3.10}$$

where f and g are arbitrary functions and c is an arbitrary constant (not necessarily real). Examples of linear operators include $\hat{x}^2$, d/dx, and d^2/dx^2. Some nonlinear operators are cos and $(\quad)^2$, where $(\quad)^2$ squares the function it acts on.

Useful identities in linear-operator manipulations are

$$(\hat{A} + \hat{B})\hat{C} = \hat{A}\hat{C} + \hat{B}\hat{C}$$ (3.11)

$$\hat{A}(\hat{B} + \hat{C}) = \hat{A}\hat{B} + \hat{A}\hat{C}$$ (3.12)

Eigenfunctions and Eigenvalues

Suppose that the effect of operating on some function $f(x)$ with the linear operator $\hat{A}$ is simply to multiply $f(x)$ by a certain constant k. We then say that $f(x)$ is an **eigenfunction** of $\hat{A}$ with **eigenvalue** k. (*Eigen* is a German word meaning *characteristic*.) As part of the definition, we shall require that the eigenfunction $f(x)$ is not identically zero. By this we mean that, although $f(x)$ may vanish at various points, it is not everywhere zero. We have

$$\hat{A}f(x) = kf(x) \qquad (3.14)$$

As an example of (3.14), e^{2x} is an eigenfunction of the operator d/dx with eigenvalue 2:

$$(d/dx)e^{2x} = 2e^{2x}$$

However, $\sin 2x$ is not an eigenfunction of d/dx, since $(d/dx)(\sin 2x) = 2 \cos 2x$, which is not a constant times $\sin 2x$.

Sir William Rowan Hamilton (1805–1865) devised an alternative form of Newton's equations of motion involving a function H, the Hamiltonian function for the system. For a system where the potential energy is a function of the coordinates only, the total energy remains constant with time; that is, E is conserved. We shall restrict ourselves to such conservative systems. For conservative systems, the classical-mechanical **Hamiltonian function** turns out to be simply the total energy expressed in terms of coordinates and conjugate momenta. For Cartesian coordinates x, y, z, the **conjugate**

momenta are the components of linear momentum in the x, y, and z directions: p_x, p_y, and p_z:

$$p_x \equiv mv_x, \quad p_y \equiv mv_y, \quad p_z \equiv mv_z \qquad (3.19)$$

where v_x, v_y, and v_z are the components of the particle's velocity in the x, y, and z directions.

Let us find the classical-mechanical Hamiltonian function for a particle of mass m moving in one dimension and subject to a potential energy $V(x)$. The Hamiltonian function is equal to the energy, which is composed of kinetic and potential energies. The familiar form of the kinetic energy, $\frac{1}{2} m v_x^2$, will not do, however, since we must express the Hamiltonian as a function of coordinates and momenta, not velocities. Since $v_x = p_x/m$, the form of the kinetic energy we want is $p_x^2/2m$. The Hamiltonian function is

$$H = \frac{p_x^2}{2m} + V(x) \tag{3.20}$$

The time-independent Schrödinger equation (3.1) indicates that, corresponding to the Hamiltonian function (3.20), we have a quantum-mechanical operator

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

Each Cartesian component of linear momentum p_q is replaced by the operator

$$\hat{p}_q = \frac{\hbar}{i}\frac{\partial}{\partial q} = -i\hbar\frac{\partial}{\partial q}$$

where $i = \sqrt{-1}$ and $\partial/\partial q$ is the operator for the partial derivative with respect to the coordinate q. Note that $1/i = i/i^2 = i/(-1) = -i$.

 Consider some examples. The operator corresponding to the x coordinate is multiplication by x:

$$\boxed{\hat{x} = x \times} \qquad (3.21)$$

Also,

$$\boxed{\hat{y} = y \times \quad \text{and} \quad \hat{z} = z \times} \qquad (3.22)$$

The operators for the components of linear momentum are

$$\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}, \quad \hat{p}_y = \frac{\hbar}{i}\frac{\partial}{\partial y}, \quad \hat{p}_z = \frac{\hbar}{i}\frac{\partial}{\partial z} \qquad (3.23)$$

The operator corresponding to p_x^2 is

$$\hat{p}_x^2 = \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 = \frac{\hbar}{i}\frac{\partial}{\partial x}\frac{\hbar}{i}\frac{\partial}{\partial x} = -\hbar^2\frac{\partial^2}{\partial x^2} \qquad (3.24)$$

with similar expressions for $\hat{p}_y^2$ and $\hat{p}_z^2$.

What are the potential-energy and kinetic-energy operators in one dimension? Suppose a system has the potential-energy function $V(x) = ax^2$, where a is a constant. Replacing x with $x \times$, we see that the potential-energy operator is simply multiplication by ax^2; that is, $\hat{V}(x) = ax^2 \times$. In general, we have for any potential-energy function

$$\hat{V}(x) = V(x) \times \qquad (3.25)$$

The classical-mechanical expression for the kinetic energy T in (3.20) is

$$T = p_x^2/2m \qquad (3.26)$$

153

Replacing p_x by the corresponding operator (3.23), we have

$$\hat{T} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \tag{3.27}$$

where (3.24) has been used, and the partial derivative becomes an ordinary derivative in one dimension. The classical-mechanical Hamiltonian (3.20) is

$$H = T + V = p_x^2/2m + V(x) \tag{3.28}$$

The corresponding quantum-mechanical Hamiltonian (or energy) operator is

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \tag{3.29}$$

which agrees with the operator in the Schrödinger equation (3.1). Note that all these operators are linear.

How are the quantum-mechanical operators related to the corresponding proper-ties of a system? Each such operator has its own set of eigenfunctions and eigenvalues. Let $\hat{B}$ be the quantum-mechanical operator that corresponds to the physical prop-erty B. Letting f_i and b_i symbolize the eigenfunctions and eigenvalues of $\hat{B}$, we have [Eq. (3.14)]

$$\hat{B}f_i = b_i f_i, \quad i = 1, 2, 3, \ldots \tag{3.30}$$

The operator $\hat{B}$ has many eigenfunctions and eigenvalues, and the subscript i is used to indicate this. $\hat{B}$ is usually a differential operator, and (3.30) is a differential equation whose solutions give the eigenfunctions and eigenvalues. Quantum mechanics postulates that (no matter what the state function of the system happens to be) *a measurement of the property B must yield one of the eigenvalues b_i of the operator $\hat{B}$.* For example, the only values that can be found for the energy of a system are the eigenvalues of the energy (Hamiltonian) operator $\hat{H}$. Using ψ_i to symbolize the eigenfunctions of $\hat{H}$, we have as the eigenvalue equation (3.30)

$$\hat{H}\psi_i = E_i\psi_i$$

(3.31)

Using the Hamiltonian (3.29) in (3.31), we obtain for a one-dimensional, one-particle system

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \right]\psi_i = E_i\psi_i \tag{3.32}$$

which is the time-independent Schrödinger equation (3.1). Thus our postulates about operators are consistent with our previous work.

In Chapter 1 we postulated that the state of a quantum-mechanical system is specified by a state function $\Psi(x, t)$, which contains all the information we can know about the system. How does Ψ give us information about the property B? We postulate that *if Ψ is an eigenfunction of $\hat{B}$ with eigenvalue b_k, then a measurement of B is certain to yield the value b_k.* Consider, for example, the energy. The eigenfunctions of the energy operator are the solutions $\psi(x)$ of the time-independent Schrödinger equation (3.32). Suppose the system is in a stationary state with state function [Eq. (1.20)]

$$\Psi(x, t) = e^{-iEt/\hbar}\psi(x) \tag{3.33}$$

Is $\Psi(x, t)$ an eigenfunction of the energy operator $\hat{H}$? We have

$$\hat{H}\Psi(x, t) = \hat{H}e^{-iEt/\hbar}\psi(x)$$

$\hat{H}$ contains no derivatives with respect to time and therefore does not affect the exponential factor $e^{-iEt/\hbar}$. We have

$$\hat{H}\Psi(x, t) = e^{-iEt/\hbar}\hat{H}\psi(x) = Ee^{-iEt/\hbar}\psi(x) = E\Psi(x, t)$$

$$\hat{H}\Psi = E\Psi \tag{3.34}$$

where (3.31) was used. Hence, for a stationary state, $\Psi(x, t)$ is an eigenfunction of $\hat{H}$, and we are certain to obtain the value E when we measure the energy.

The Three-Dimensional, Many-Particle Schrödinger Equation:

Up to now we have restricted ourselves to one-dimensional, one-particle systems. The operator formalism developed in the last section allows us to extend our work to three dimensional, many-particle systems. The time-dependent Schrödinger equation for the time development of the state function is postulated to have the form of Eq. (1.13):

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi \qquad (3.42)$$

The time-independent Schrödinger equation for the energy eigenfunctions and eigenvalues is:

$$\hat{H}\psi = E\psi \qquad\qquad (3.43)$$

which is obtained from (3.42) by taking the potential energy as independent of time and applying the separation-of-variables procedure used to obtain (1.19) from (1.13).

For a one-particle, three-dimensional system, the classical-mechanical Hamiltonian is:

$$H = T + V = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V(x, y, z) \qquad (3.44)$$

Introducing the quantum-mechanical operators [Eq. (3.24)], we have for the Hamiltonian operator:

$$\hat{p}_x^2 = \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 = \frac{\hbar}{i}\frac{\partial}{\partial x}\frac{\hbar}{i}\frac{\partial}{\partial x} = -\hbar^2\frac{\partial^2}{\partial x^2} \qquad (3.24)$$

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x, y, z) \qquad (3.45)$$

163

The operator in parentheses in (3.45) is called the **Laplacian operator** ∇^2 (read as "del squared"):

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad (3.46)$$

The one-particle, three-dimensional, time-independent Schrödinger equation is then:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \qquad (3.47)$$

Now consider a three-dimensional system with n particles. Let particle i have mass m_i and coordinates (x_i, y_i, z_i), where i = 1, 2, 3, …, n. The kinetic energy is the sum of the kinetic energies of the individual particles:

$$T = \frac{1}{2m_1}(p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2) + \frac{1}{2m_2}(p_{x_2}^2 + p_{y_2}^2 + p_{z_2}^2) + \cdots + \frac{1}{2m_n}(p_{x_n}^2 + p_{y_n}^2 + p_{z_n}^2)$$

where p_{xi} is the x component of the linear momentum of particle i, and so on. The kinetic energy operator is:

$$\hat{T} = -\frac{\hbar^2}{2m_1}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}\right) - \cdots - \frac{\hbar^2}{2m_n}\left(\frac{\partial^2}{\partial x_n^2} + \frac{\partial^2}{\partial y_n^2} + \frac{\partial^2}{\partial z_n^2}\right)$$

$$\hat{T} = -\sum_{i=1}^{n}\frac{\hbar^2}{2m_i}\nabla_i^2 \qquad (3.48)$$

$$\nabla_i^2 \equiv \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \qquad (3.49)$$

We shall usually restrict ourselves to cases where the potential energy depends only on the 3n coordinates:

$$V = V(x_1, y_1, z_1, \ldots, x_n, y_n, z_n)$$

The Hamiltonian operator for an n-particle, three-dimensional system is then

$$\hat{H} = -\sum_{i=1}^{n} \frac{\hbar^2}{2m_i} \nabla_i^2 + V(x_1, \ldots, z_n) \qquad (3.50)$$

and the time-independent Schrödinger equation is:

$$\left[-\sum_{i=1}^{n} \frac{\hbar^2}{2m_i} \nabla_i^2 + V(x_1, \ldots, z_n) \right] \psi = E\psi \qquad (3.51)$$

where the time-independent wave function is a function of the 3n coordinates of the n particles:

$$\psi = \psi(x_1, y_1, z_1, \ldots, x_n, y_n, z_n) \qquad (3.52)$$

The Schrödinger equation (3.51) is a linear partial differential equation.

The Hartree–Fock Self-Consistent-Field Method:

For the hydrogen atom, the exact wave function is known. For helium and lithium, very accurate wave functions have been calculated by including inter electronic distances in the variation functions. For atoms of higher atomic number, one way to find an accurate wave function is to first find an approximate wave function using the Hartree–Fock procedure, which we shall outline in this section. The Hartree–Fock method is the basis for the use of atomic and molecular orbitals in many-electron systems.

The Hamiltonian operator for an n-electron atom is:

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{n} \nabla_i^2 - \sum_{i=1}^{n} \frac{Ze^2}{4\pi\varepsilon_0 r_i} + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \qquad (11.1)$$

where an infinitely heavy point nucleus was assumed. The first sum in (11.1) contains the kinetic-energy operators for the n electrons. The second sum is the potential energy for the attractions between the electrons and the nucleus of charge Ze.

For a neutral atom, $Z = n$. The last sum is the potential energy of the inter electronic repulsions. The restriction $j > i$ avoids counting each inter electronic repulsion twice and avoids terms like $e^2/4\pi\varepsilon_0 r_{ii}$. The Hamiltonian (11.1) is incomplete, because it omits spin–orbit and other interactions. The omitted terms are small (except for atoms with high Z).