Perturbation Treatment of the Helium-Atom Ground state:

The helium atom has two electrons and a nucleus of charge +2e. We shall consider the nucleus to be at rest and place the origin of the coordinate system at the nucleus. The coordinates of electrons 1 and 2 are (x_1, y_1, z_1) and (x_2, y_2, z_2); see Fig. 9.1.

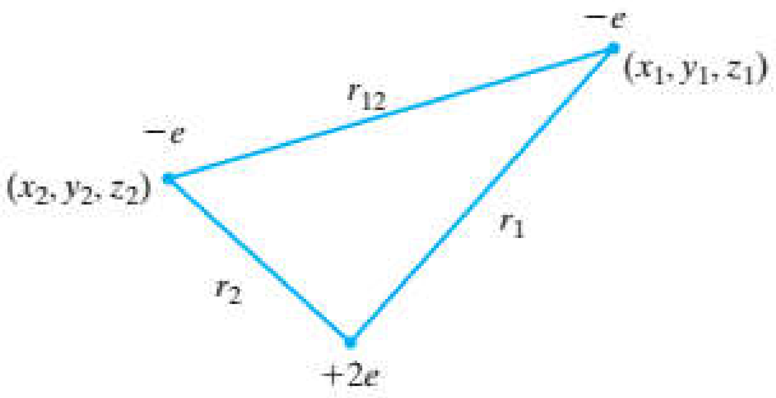
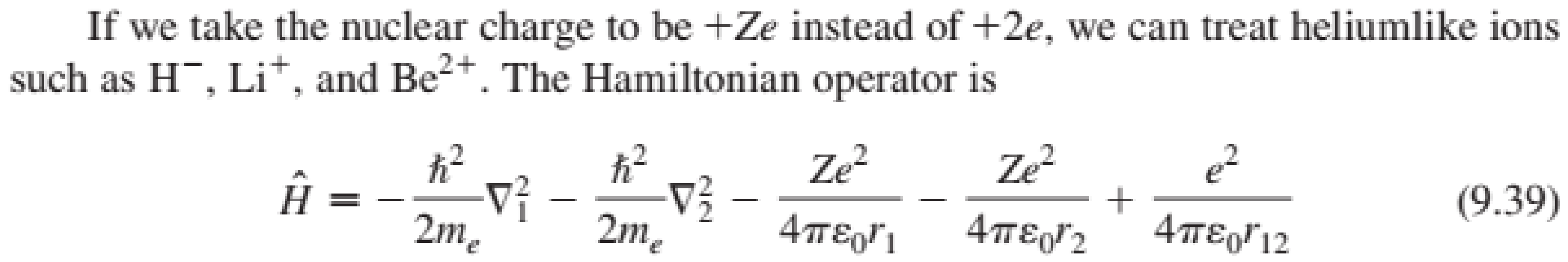


FIGURE 9.1 Interparticle distances in the helium atom.



If we take the nuclear charge to be $+Ze$ instead of $+2e$, we can treat heliumlike ions such as H^-, Li^+, and Be^{2+}. The Hamiltonian operator is

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}} \tag{9.39}$$

where m_e is the mass of the electron, r_1 and r_2 are the distances of electrons 1 and 2 from the nucleus, and r_{12} is the distance from electron 1 to 2. The first two terms are the operators for the electrons' kinetic energy. The third and fourth terms are the potential energies of attraction between the electrons and the nucleus. The final term is the potential energy of inter electronic repulsion. Note that the potential energy of a system of interacting particles cannot be written as the sum of potential energies of the individual particles. The potential energy is a property of the system as a whole.

$$-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$$

$$\boxed{\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}}$$

$$x = r\sin\theta\cos\phi, \qquad y = r\sin\theta\sin\phi, \qquad z = r\cos\theta \tag{5.51}$$

$$r^2 = x^2 + y^2 + z^2, \qquad \cos\theta = \frac{z}{(x^2 + y^2 + z^2)^{1/2}}, \qquad \tan\phi = \frac{y}{x} \tag{5.52}$$

$$\frac{\partial}{\partial x} = \left(\frac{\partial r}{\partial x}\right)_{y,z}\frac{\partial}{\partial r} + \left(\frac{\partial \theta}{\partial x}\right)_{y,z}\frac{\partial}{\partial \theta} + \left(\frac{\partial \phi}{\partial x}\right)_{y,z}\frac{\partial}{\partial \phi} \tag{5.56}$$

$$\left(\frac{\partial r}{\partial x}\right)_{y,z} = \sin\theta\cos\phi \tag{5.57}$$

$$\left(\frac{\partial r}{\partial y}\right)_{x,z} = \sin\theta\sin\phi, \qquad \left(\frac{\partial r}{\partial z}\right)_{x,y} = \cos\theta \tag{5.58}$$

$$\left(\frac{\partial \theta}{\partial x}\right)_{y,z} = \frac{\cos\theta\cos\phi}{r} \tag{5.59}$$

$$\left(\frac{\partial \theta}{\partial y}\right)_{x,z} = \frac{\cos\theta\sin\phi}{r}, \qquad \left(\frac{\partial \theta}{\partial z}\right)_{x,y} = -\frac{\sin\theta}{r} \tag{5.60}$$

$$\left(\frac{\partial \phi}{\partial x}\right)_{y,z} = -\frac{\sin\phi}{r\sin\theta}, \qquad \left(\frac{\partial \phi}{\partial y}\right)_{x,z} = \frac{\cos\phi}{r\sin\theta}, \qquad \left(\frac{\partial \phi}{\partial z}\right)_{x,y} = 0 \tag{5.61}$$

Substituting (5.57), (5.59), and (5.61) into (5.56), we find

$$\frac{\partial}{\partial x} = \sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi} \tag{5.62}$$

Similarly,

$$\frac{\partial}{\partial y} = \sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi} \tag{5.63}$$

$$\frac{\partial}{\partial z} = \cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta} \tag{5.64}$$

Angular Momentum of a One-Particle System

we found the eigenfunctions and eigenvalues for the linear-momentum operator $\hat{p}_x$. In this section we consider the same problem for the angular momentum of a particle. Angular momentum plays a key role in the quantum mechanics of atomic structure. We begin by reviewing the classical mechanics of angular momentum.

Classical mechanics of One-particle angular momentum:

Consider a moving particle of mass m. We set up a Cartesian coordinate system that is fixed in space. Let r be the vector from the origin to the instantaneous position of the particle. We have:

$$\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z \tag{5.33}$$

where x, y, and z are the particle's coordinates at a given instant.

Defining the velocity vector v as the time derivative of the position vector, we have:

$$\mathbf{v} \equiv \frac{d\mathbf{r}}{dt} = \mathbf{i}\,\frac{dx}{dt} + \mathbf{j}\,\frac{dy}{dt} + \mathbf{k}\,\frac{dz}{dt} \tag{5.34}$$

$$v_x = dx/dt, \quad v_y = dy/dt, \quad v_z = dz/dt$$

We define the particle's **linear momentum** vector **p** by

$$\boxed{\mathbf{p} \equiv m\mathbf{v}} \tag{5.35}$$

$$p_x = mv_x, \quad p_y = mv_y, \quad p_z = mv_z \tag{5.36}$$

The particle's **angular momentum L** with respect to the coordinate origin is defined in classical mechanics as

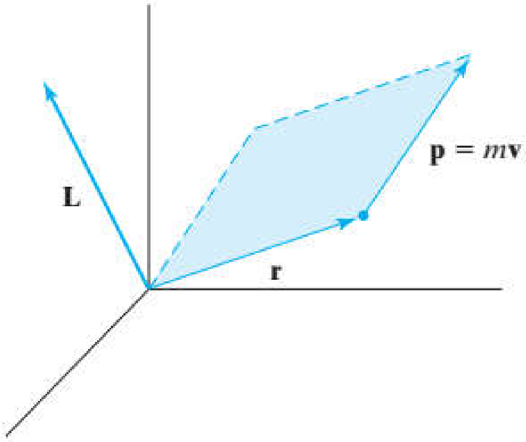
$$\boxed{\mathbf{L} \equiv \mathbf{r} \times \mathbf{p}} \qquad \textbf{(5.37)}$$

$$\mathbf{L} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} \qquad (5.38)$$

$$L_x = yp_z - zp_y, \quad L_y = zp_x - xp_z, \quad L_z = xp_y - yp_x \qquad (5.39)$$

where (5.28) was used. L_x, L_y, and L_z are the components of **L** along the x, y, and z axes. The angular-momentum vector **L** is perpendicular to the plane defined by the particle's position vector **r** and its velocity **v** (Fig. 5.4).

FIGURE 5.4 $\mathbf{L} \equiv \mathbf{r} \times \mathbf{p}$.



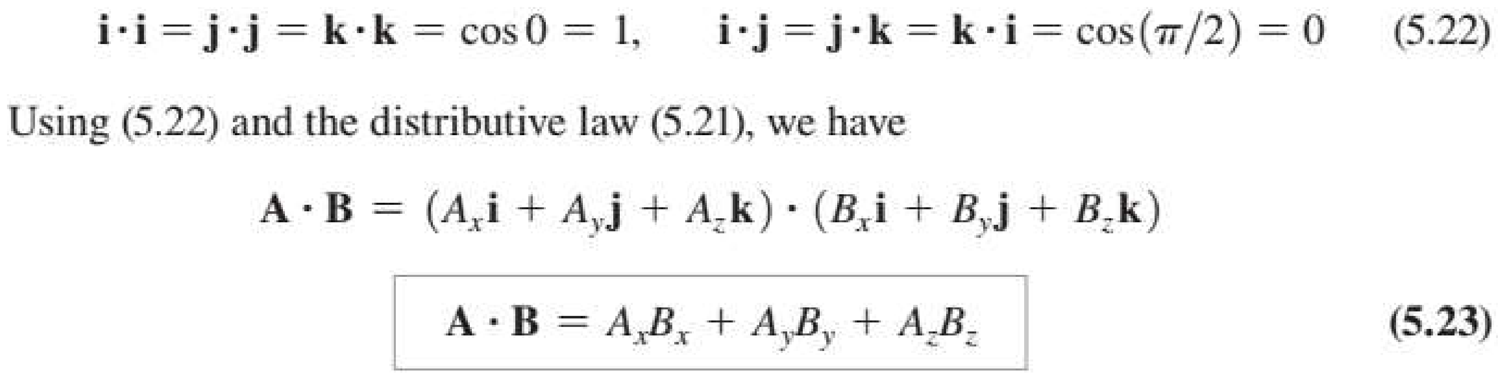
$$\mathbf{A} \times \mathbf{B} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ A_x & A_y & A_z \\ B_x & B_y & B_z \end{vmatrix} = \mathbf{i}\begin{vmatrix} A_y & A_z \\ B_y & B_z \end{vmatrix} - \mathbf{j}\begin{vmatrix} A_x & A_z \\ B_x & B_z \end{vmatrix} + \mathbf{k}\begin{vmatrix} A_x & A_y \\ B_x & B_y \end{vmatrix}$$

The *torque* τ acting on a particle is defined as the cross product of **r** and the force **F** acting on the particle: $\tau \equiv \mathbf{r} \times \mathbf{F}$. One can show that $\tau = d\mathbf{L}/dt$. When no torque acts on a particle, the rate of change of its angular momentum is zero; that is, its angular momentum is constant (or conserved). For a planet orbiting the sun, the gravitational force is radially directed. Since the cross product of two parallel vectors is zero, there is no torque on the planet and its angular momentum is conserved.

One-particle Orbital-angular-momentum Operators:

Now let us turn to the quantum-mechanical treatment. In quantum mechanics, there are two kinds of angular momenta. Orbital angular momentum results from the motion of a particle through space, and is the analog of the classical-mechanical quantity L. Spin angular momentum is an intrinsic property of many microscopic particles and has no classical-mechanical analog. We are now considering only orbital angular momentum.

We get the quantum-mechanical operators for the components of orbital angular momentum of a particle by replacing the coordinates and momenta in the classical equations (5.39) by their corresponding operators. We find:



$$\mathbf{i}\cdot\mathbf{i} = \mathbf{j}\cdot\mathbf{j} = \mathbf{k}\cdot\mathbf{k} = \cos 0 = 1, \qquad \mathbf{i}\cdot\mathbf{j} = \mathbf{j}\cdot\mathbf{k} = \mathbf{k}\cdot\mathbf{i} = \cos(\pi/2) = 0 \tag{5.22}$$

Using (5.22) and the distributive law (5.21), we have

$$\mathbf{A}\cdot\mathbf{B} = (A_x\mathbf{i} + A_y\mathbf{j} + A_z\mathbf{k})\cdot(B_x\mathbf{i} + B_y\mathbf{j} + B_z\mathbf{k})$$

$$\boxed{\mathbf{A}\cdot\mathbf{B} = A_xB_x + A_yB_y + A_zB_z} \tag{5.23}$$

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

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

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

$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \tag{5.40}$$

$$\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \tag{5.41}$$

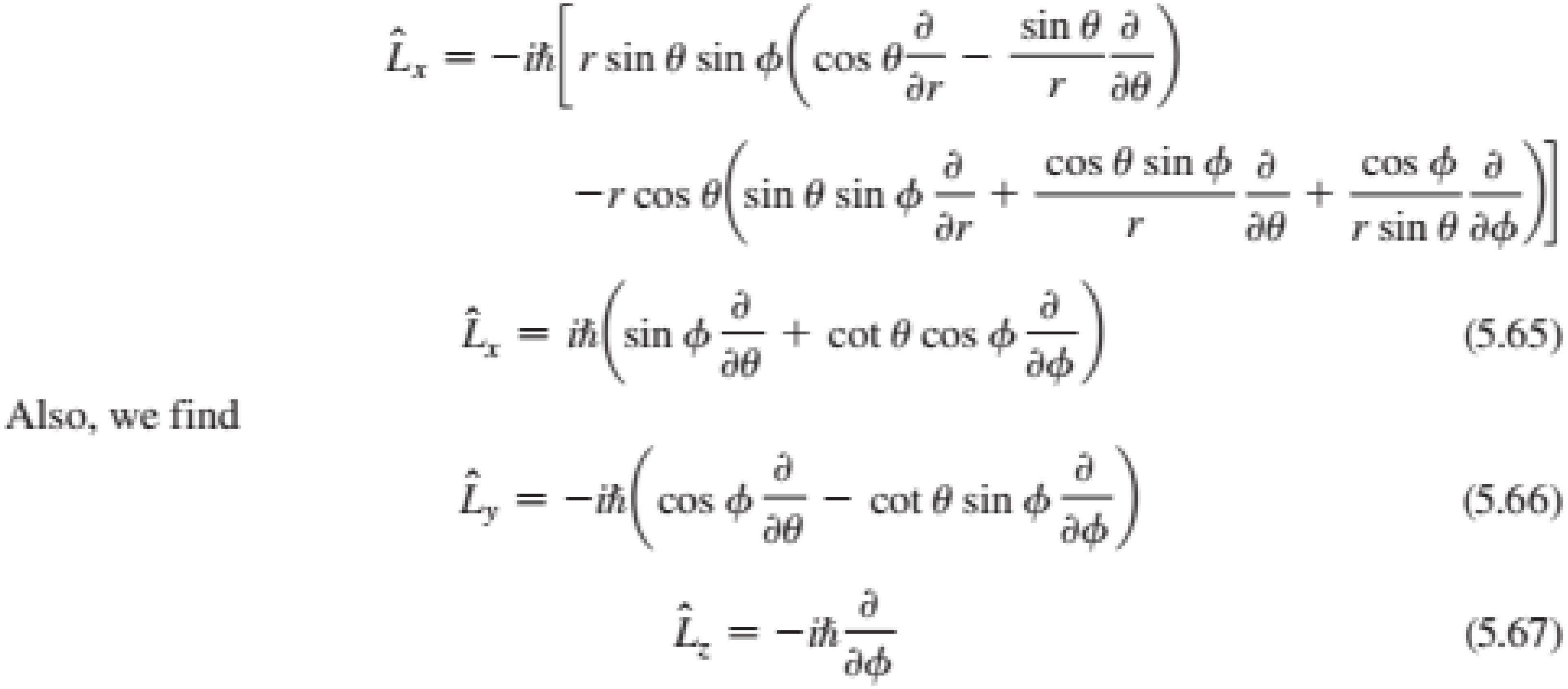
$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \tag{5.42}$$

(Since $\hat{y}\hat{p}_z = \hat{p}_z\hat{y}$, and so on, we do not run into any problems of noncommutativity in constructing these operators.) Using

$$\hat{L}^2 = |\hat{\mathbf{L}}|^2 = \hat{\mathbf{L}} \cdot \hat{\mathbf{L}} = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \tag{5.43}$$

we can construct the operator for the square of the angular-momentum magnitude from the operators in (5.40)–(5.42).

At last, we are ready to express the angular-momentum components in spherical coordinates. Substituting (5.51), (5.63), and (5.64) into (5.40), we have:



$$\hat{L}_x = -i\hbar\left[r\sin\theta\sin\phi\left(\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right)\right.$$
$$\left. - r\cos\theta\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\right]$$

$$\hat{L}_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \qquad (5.65)$$

Also, we find

$$\hat{L}_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \qquad (5.66)$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi} \qquad (5.67)$$

By squaring each of $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ and then adding their squares, we can construct $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ [Eq. (5.43)]. The result is (Prob. 5.17)

$$\hat{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) \qquad (5.68)$$

Although the angular-momentum operators depend on all three Cartesian coordinates, x, y, and z, they involve only the two spherical coordinates θ and ϕ.

We already have the forms of the operators ∂/∂x, ∂/∂y, and ∂/∂z in these coordinates [Eqs. (5.62)–(5.64)], and by squaring each of these operators and then adding their squares, we get the Laplacian. This calculation is left as an exercise. The result is:

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2}\cot\theta\frac{\partial}{\partial \theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial \phi^2} \qquad (6.6)$$

Looking back to (5.68), which gives the operator L^2 for the square of the magnitude of the orbital angular momentum of a single particle, we see that:

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{1}{r^2\hbar^2}\hat{L}^2 \tag{6.7}$$

The Hamiltonian (6.5) becomes:

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{1}{2mr^2}\hat{L}^2 + V(r) \tag{6.8}$$

The eigenfunctions of $\hat{L}^2$ are the spherical harmonics $Y_l^m(\theta, \phi)$, and since $\hat{L}^2$ does not involve r, we can multiply Y_l^m by an arbitrary function of r and still have eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$. Therefore,

$$\boxed{\psi = R(r)Y_l^m(\theta, \phi)} \tag{6.16}$$

The Schrödinger equation involves six independent variables, three coordinates for each electron. In spherical coordinates, $\psi = \psi(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$.

The operator ∇_1^2 is given by Eq. (6.6) with r_1, θ_1, ϕ_1 replacing r, θ, ϕ. The variable r_{12} is $r_{12} = \left[(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2\right]^{1/2}$, and by using the relations between Cartesian and spherical coordinates, we can express r_{12} in terms of $r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2$.

Because of the $e^2/4\pi\varepsilon_0 r_{12}$ term, the Schrödinger equation for helium cannot be separated in any coordinate system, and we must use approximation methods. The perturbation method separates the Hamiltonian (9.39) into two parts, $\hat{H}^0$ and $\hat{H}'$, where $\hat{H}^0$ is the Hamiltonian of an exactly solvable problem. If we choose

$$\hat{H}^0 = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_2} \qquad (9.40)$$

$$\hat{H}' = \frac{e^2}{4\pi\varepsilon_0 r_{12}} \qquad (9.41)$$

then $\hat{H}^0$ is the sum of two hydrogenlike Hamiltonians, one for each electron:

$$\hat{H}^0 = \hat{H}_1^0 + \hat{H}_2^0 \tag{9.42}$$

$$\hat{H}_1^0 \equiv -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1}, \quad \hat{H}_2^0 \equiv -\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_2} \tag{9.43}$$

The unperturbed system is a helium atom in which the two electrons exert no forces on each other. Although such a system does not exist, this does not prevent us from applying perturbation theory to this system.

Since the unperturbed Hamiltonian (9.42) is the sum of the Hamiltonians for two independent particles, we can use the separation-of-variables results of Eqs. (6.18) to (6.24) to conclude that the unperturbed wave functions have the form

$$\psi^{(0)}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) = F_1(r_1, \theta_1, \phi_1)F_2(r_2, \theta_2, \phi_2) \tag{9.44}$$

and the unperturbed energies are

$$E^{(0)} = E_1 + E_2 \tag{9.45}$$

$$\hat{H}_1^0 F_1 = E_1 F_1, \qquad \hat{H}_2^0 F_2 = E_2 F_2 \tag{9.46}$$

Noninteracting Particles and Separation of Variables:

Up to this point, we have solved only one-particle quantum-mechanical problems. The hydrogen atom is a two-particle system, and as a preliminary to dealing with the H atom, we first consider a simpler case, that of two noninteracting particles.

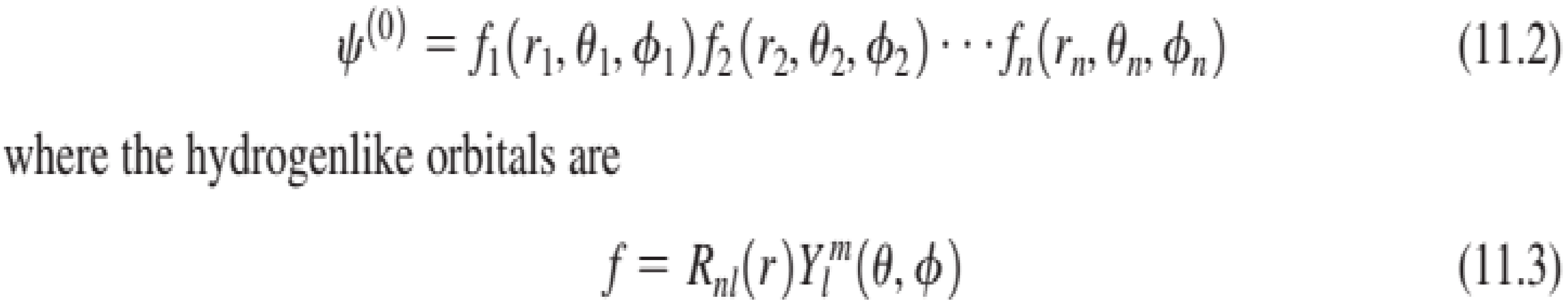
Suppose that a system is composed of the noninteracting particles 1 and 2. Let q_1 and q_2 symbolize the coordinates (x_1, y_1, z_1) and (x_2, y_2, z_2) of particles 1 and 2. Because the particles exert no forces on each other, the classical-mechanical energy of the system is the sum of the energies of the two particles: $E = E_1 + E_2 = T_1 + V_1 + T_2 + V_2$, and the classical Hamiltonian is the sum of Hamiltonians for each particle: $H = H_1 + H_2$. Therefore, the Hamiltonian operator is:

$$\hat{H} = \hat{H}_1 + \hat{H}_2$$

where $\hat{H}_1$ involves only the coordinates q_1 and the momentum operators $\hat{p}_1$ that correspond to q_1. The Schrödinger equation for the system is

$$(\hat{H}_1 + \hat{H}_2)\psi(q_1, q_2) = E\psi(q_1, q_2) \tag{6.18}$$

The Hartree SCF Method: Because of the inter electronic repulsion terms $e^2>4\pi\varepsilon_0 r_{ii}$, the Schrödinger equation for an atom is not separable. Recalling the perturbation treatment of helium, we can obtain a zeroth-order wave function by neglecting these repulsions. The Schrödinger equation would then separate into n one-electron hydrogen like equations. The zeroth-order wave function would be a product of n hydrogen like (one-electron) orbitals:



$$\psi^{(0)} = f_1(r_1, \theta_1, \phi_1) f_2(r_2, \theta_2, \phi_2) \cdots f_n(r_n, \theta_n, \phi_n) \tag{11.2}$$

where the hydrogenlike orbitals are

$$f = R_{nl}(r) Y_l^m(\theta, \phi) \tag{11.3}$$

The Born–Oppenheimer Approximation:

If we assume the nuclei and electrons to be point masses and neglect spin–orbit and other relativistic interactions (Sections 11.6 and 11.7), then the molecular Hamiltonian operator is:

$$\hat{H} = -\frac{\hbar^2}{2}\sum_{\alpha}\frac{1}{m_\alpha}\nabla_\alpha^2 - \frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_\alpha \sum_{\beta>\alpha}\frac{Z_\alpha Z_\beta e^2}{4\pi\varepsilon_0 r_{\alpha\beta}} - \sum_\alpha \sum_i \frac{Z_\alpha e^2}{4\pi\varepsilon_0 r_{i\alpha}} + \sum_j \sum_{i>j}\frac{e^2}{4\pi\varepsilon_0 r_{ij}} \tag{13.1}$$

where α and β refer to nuclei and i and j refer to electrons. The first term in (13.1) is the operator for the kinetic energy of the nuclei. The second term is the operator for the kinetic energy of the electrons. The third term is the potential energy of the repulsions between the nuclei, $r_{\alpha\beta}$ being the distance between nuclei α and β with atomic numbers Z_α and Z_β. The fourth term is the potential energy of the attractions between the electrons and the nuclei, ria being the distance between electron i and nucleus α. The last term is the potential energy of the repulsions between the electrons, r_{ij} being the distance between electrons i and j. The zero level of potential energy for (13.1) corresponds to having all the charges (electrons and nuclei) infinitely far from one another.

As an example, consider H_2. Let α and β be the two protons, 1 and 2 be the two electrons, and m_p be the proton mass. The H_2 molecular Hamiltonian operator is:

$$\hat{H} = -\frac{\hbar^2}{2m_p}\nabla_\alpha^2 - \frac{\hbar^2}{2m_p}\nabla_\beta^2 - \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 + \frac{e^2}{4\pi\varepsilon_0 r_{\alpha\beta}} - \frac{e^2}{4\pi\varepsilon_0 r_{1\alpha}} - \frac{e^2}{4\pi\varepsilon_0 r_{1\beta}} - \frac{e^2}{4\pi\varepsilon_0 r_{2\alpha}} - \frac{e^2}{4\pi\varepsilon_0 r_{2\beta}} + \frac{e^2}{4\pi\varepsilon_0 r_{12}} \qquad (13.2)$$

The wave functions and energies of a molecule are found from the Schrödinger equation:

$$\hat{H}\psi(q_i, q_\alpha) = E\psi(q_i, q_\alpha) \qquad (13.3)$$

where q_i and q_α symbolize the electronic and nuclear coordinates, respectively.

The molecular Hamiltonian (13.1) is formidable enough to terrify any quantum chemist. Fortunately, a very accurate, simplifying approximation exists. Since nuclei are much heavier than electrons ($m_\alpha >> m_e$), the electrons move much faster than the nuclei. Hence, to a good approximation as far as the electrons are concerned, we can regard the nuclei as fixed while the electrons carry out their motions. Speaking classically, during the time of a cycle of electronic motion, the change in nuclear configuration is negligible. Thus, considering the nuclei as fixed, we omit the nuclear kinetic-energy terms from (13.1) to obtain the Schrödinger equation for electronic motion:

$$\boxed{(\hat{H}_{el} + V_{NN})\psi_{el} = U\psi_{el}} \qquad \textbf{(13.4)}$$

where the **purely electronic Hamiltonian** $\hat{H}_{\text{el}}$ is

$$\hat{H}_{\text{el}} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_\alpha \sum_i \frac{Z_\alpha e^2}{4\pi\varepsilon_0 r_{i\alpha}} + \sum_j \sum_{i>j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \qquad (13.5)$$

The electronic Hamiltonian including nuclear repulsion is $\hat{H}_{\text{el}} + V_{NN}$. The nuclear-repulsion term V_{NN} is

$$V_{NN} = \sum_\alpha \sum_{\beta>\alpha} \frac{Z_\alpha Z_\beta e^2}{4\pi\varepsilon_0 r_{\alpha\beta}} \qquad (13.6)$$

The energy U in (13.4) is the electronic energy including internuclear repulsion. The internuclear distances $r_{\alpha\beta}$ in (13.4) are not variables, but are each fixed at some constant value. Of course, there are an infinite number of possible nuclear configurations, and for each of these we may solve the electronic Schrödinger equation (13.4) to get a set of electronic wave functions and corresponding electronic energies. Each member of the set corresponds to a different molecular electronic state. The electronic wave functions and energies thus depend parametrically on the nuclear coordinates:

$$\psi_{\text{el}} = \psi_{\text{el},n}(q_i; q_\alpha) \quad \text{and} \quad U = U_n(q_\alpha)$$

where n symbolizes the electronic quantum numbers.

The variables in the electronic Schrödinger equation (13.4) are the electronic coordinates. The quantity V_{NN} is independent of these coordinates and is a constant for a given nuclear configuration. Now it is easily proved that the omission of a constant term C from the Hamiltonian does not affect the wave functions and simply decreases each energy eigenvalue by C. Hence, if V_{NN} is omitted from (13.4), we get:

$$\hat{H}_{\text{el}}\psi_{\text{el}} = E_{\text{el}}\psi_{\text{el}} \qquad (13.7)$$

where the purely electronic energy $E_{el}(q_\alpha)$ (which depends parametrically on the nuclear coordinates q_α) is related to the electronic energy including internuclear repulsion by:

$$U = E_{\text{el}} + V_{NN} \tag{13.8}$$

We can therefore omit the internuclear repulsion from the electronic Schrödinger equation. After finding E_{el} for a particular configuration of the nuclei by solving (13.7), we calculate U using (13.8), where the constant V_{NN} is easily calculated from (13.6) using the assumed nuclear locations.

Hence the Schrödinger equation for nuclear motion is:

$$\boxed{\hat{H}_N \psi_N = E\psi_N} \qquad \textbf{(13.10)}$$

$$\hat{H}_N = -\frac{\hbar^2}{2}\sum_\alpha \frac{1}{m_\alpha}\nabla_\alpha^2 + U(q_\alpha) \qquad (13.11)$$

The variables in the nuclear Schrödinger equation are the nuclear coordinates, symbolized by q_α. The energy eigenvalue E in (13.10) is the total energy of the molecule, since the Hamiltonian (13.11) includes operators for both nuclear energy and electronic energy. E is simply a number and does not depend on any coordinates. Note that for each electronic state of a molecule we must solve a different nuclear Schrödinger equation, since U differs from state to state.

The total energy E for an electronic state of a diatomic molecule is approximately the sum of electronic, vibrational, rotational, and translational energies:

$$E \approx E_{elec} + E_{vib} + E_{rot} + E_{tr}$$

where the constant E_{elec} [not to be confused with E_{el} in (13.7)] is given by $E_{elec} = U(R_e)$.

The approximation of separating electronic and nuclear motions is called the Born–Oppenheimer approximation and is basic to quantum chemistry. Born and Oppenheimer's mathematical treatment indicated that the true molecular wave function is adequately approximated as:

$$\psi(q_i, q_\alpha) = \psi_{\mathrm{el}}(q_i; q_\alpha)\psi_N(q_\alpha) \tag{13.12}$$

if $(m_e/m_\alpha)^{1/4} \ll 1.$

The Born–Oppenheimer approximation introduces little error for the ground electronic states of diatomic molecules. Corrections for excited electronic states are larger than for the ground state, but still are usually small as compared with the errors introduced by the approximations used to solve the electronic Schrödinger equation of a many-electron molecule. Hence we shall not worry about corrections to the Born–Oppenheimer approximation.

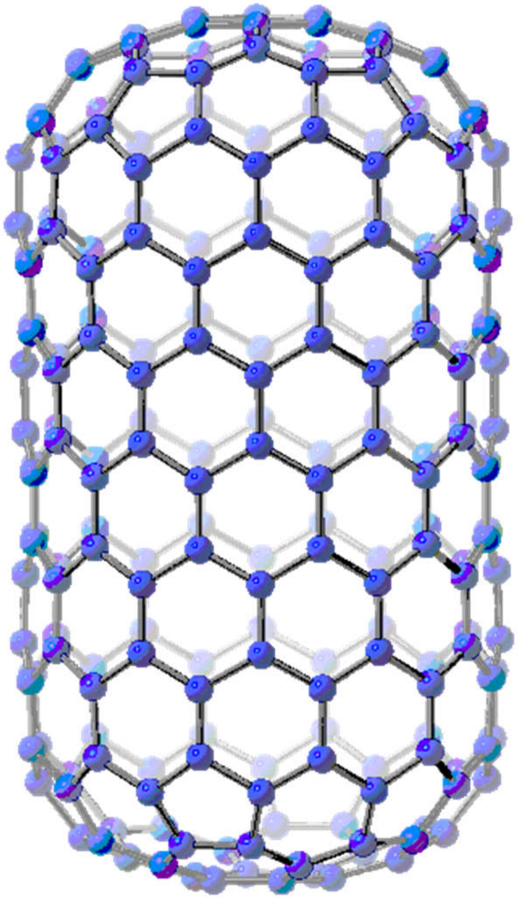
Computational Models

- A model is a system of equations, or computations used to determine the energetics of a molecule
- Different models use different approximations (or levels of theory) to produce results of varying levels of accuracy.
- There is a trade off between accuracy and computational time.
- There are two main types of models; those that use Schrödinger's equation (or simplifications of it) and those that do not.

- Types of Models

  (Listed in order from most to least accurate)

  - ***Ab initio***
    - uses Schrödinger's equation, but with approximations
  - **Semi Empirical**
    - uses experimental parameters and extensive simplifications of Schrödinger's equation
  - **Molecular Mechanics**
    - does not use Schrödinger's equation



Ab Initio:

- *Ab initio* translated from Latin means *“from first principles.”* This refers to the fact that no experimental data is used and computations are based on quantum mechanics.

- Different Levels of *Ab Initio* Calculations
  - Hartree-Fock (HF)
    - The simplest *ab initio* calculation
    - The major disadvantage of HF calculations is that electron correlation is not taken into consideration.
  - The Møller-Plesset Perturbation Theory (MP)
  - Density Functional Theory (DFT)
  - Configuration Interaction (CI)

Take into consideration electron correlation

Hartree Fock Theory

- Using MO theory, define simplified wave functions (Hartree-Fock wave functions) which can be further broken down into a linear combination of one-electron atomic orbitals (LCAO-MO).
- Choice of atomic orbitals is important since they define the basis set (gaussian type orbitals)
- Take a linear combination of gaussian orbitals to define electron conditions. (Noble Prize to John Pople 1998)
- Use Self Consistent Field Method to calculate total electronic Energy

Limitations of Hartree Fock:

- Use of simplified wave function
- Single assignment of electrons to orbitals
  - Need to expand on the configuration interaction of electrons
- Other *ab initio* methods
  - Moller-Plesset Perturbation Theory
    - Typically terminated at the second order
      - MP2, MP4

Semi-Empirical Methods:

- Use simplifying assumptions to solve the energy and wave function of molecular systems.
- Use simpler Hamiltonian operator
- Use empirical parameters for some of the two-electron integrals
- Complete or partial neglect of other electron integrals

Semi-Empirical Methods:

- CNDO – Complete Neglect of Differential Overlap
  - Bonding not calculated
- MINDO – Modified Intermediate Neglect of Differential Overlap
- MNDO – Modified Neglect of Differential Overlap

- Allow for faster calculations
- Allow for bigger chemical systems
- Obvious problems with accuracy

Semi-Empirical Methods

- Advantage
  - Faster than *ab initio*
  - Less sensitive to parameterization than MM methods
- Disadvantage
  - Accuracy depends upon parameterization

Semi-Empirical Methods

- Ignore Core Electrons
- Approximate part of HF integration

Semi-Empirical Methods

- AM1
  - Modified nuclear repulsion terms model to account for H-bonding (1985, Dewar et al)
  - Widely used today (transition metals, inorganics)

- PM3 (1989, Stewart)
  - Larger data set for parameterization compared to AM1
  - Widely used today (transition metals, inorganics)

General Reccommendations

- More accurate than empirical methods
- Less accurate than ab initio methods
- Inorganics and transition metals
- Pretty good geometry OR energies
- Poor results for systems with diffusive interactions (van der Waals, H-bonded, radicals etc.)

Density Functional Theory

- Replace complicated multi-electron wave function and the Schrodinger equation with simpler equation for calculation of electron density of the molecular system.
- Local density approximation where electronic properties are determined as functions of the electron density through the use of local relationships.
- Nobel Prize to Walter Kohn in 1998

- One to one correspondence between ground state wave function and ground state electron density
- Simpler to calculate G. S. electronic wave function from G. S. electronic density
- Faster and greater Accuracy than conventional *ab initio*
- Problematic with excited state systems
- Newest method – not standardized

Molecular Mechanics:

- Molecular mechanics programs use equations based on classical physics to calculate force fields.
- Atoms treated as spheres, bonds as springs and electron are ignored.
- It assume that the total potential energy (E_{total}) of molecule is given by sum of all the energies of attractive and repulsive forces between atom in structure.

The molecular mechanics equation:

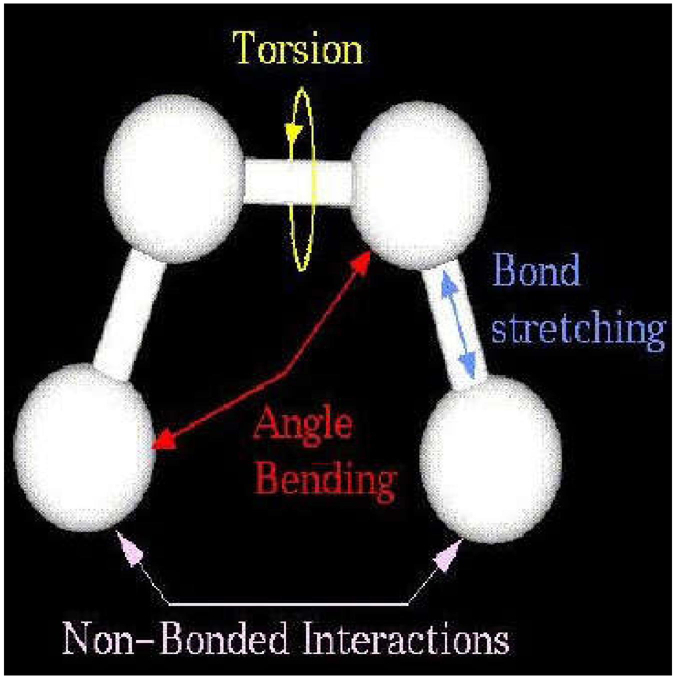
$E = E_B + E_A + E_D + E_{NB}$

E_B = The energy involved in the deformation bond either by stretching or compression.

E_A = The energy involved in the angle bending .

E_D = The torsional angle energy.

E_{NB} = The energy involved in the interaction between atoms that are not directly bonded.



Force Field:

Force field refers to calculation of the interaction and energies between different atoms between bond stretching, angle bending, torsional angle and nonbonded interaction.

Force field ignores the electronic distribution while Quantum mechanics considers electronic distribution of molecule.

Molecular Mechanics

- Based on Born-Oppenheimer Approximation
  - Electrons move in stationary field of the nuclei; electronic and nuclear motion are separable
  - Calculating position of nuclei only

Molecular Mechanics

- Classical mechanics approach
  - Develop a set of potential functions called the force field which contains adjustable parameters that are optimized to obtain the best match to the experimental properties.
- Mathematical approach in an attempt to reproduce molecular structures, potential energies and other features

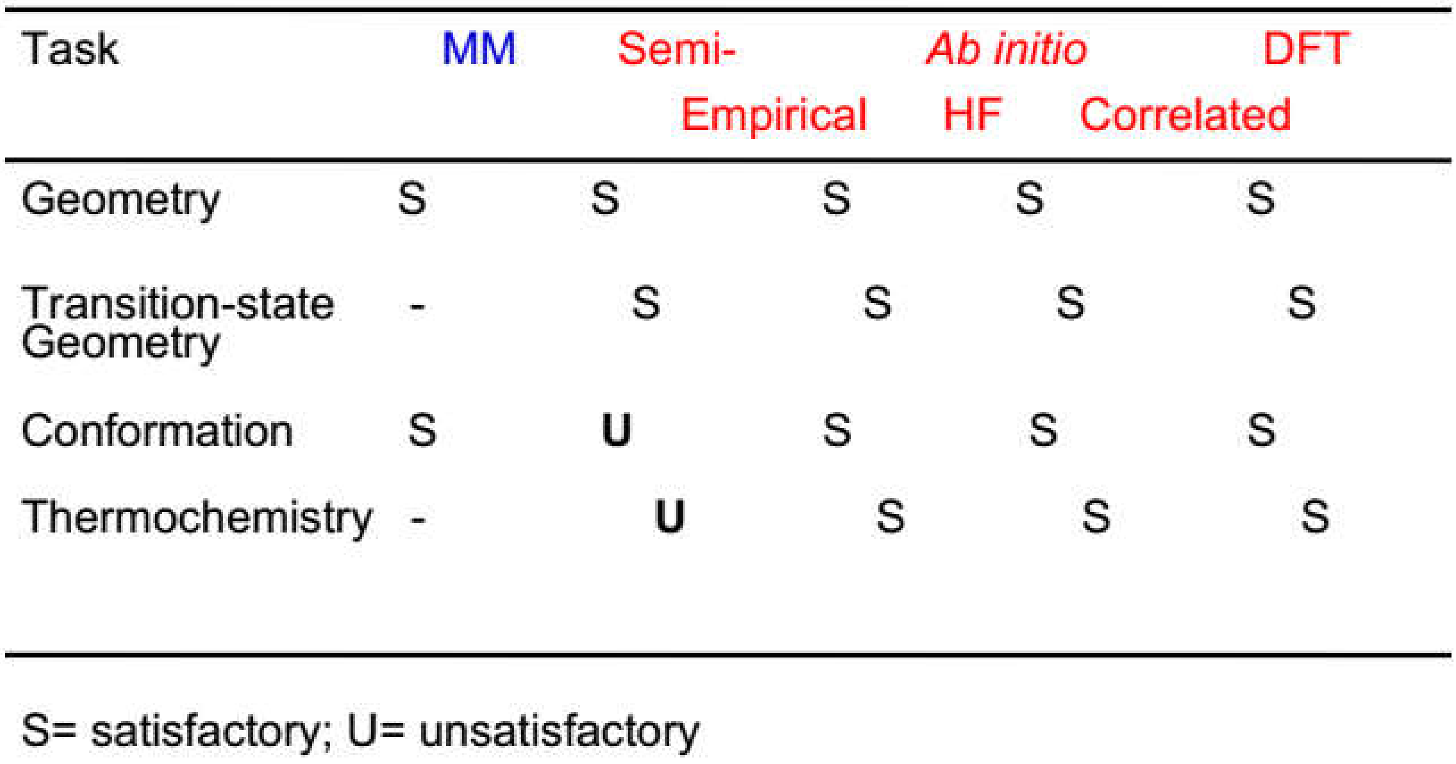
Limitations of Molecular Mechanics

- Parameters for a particular class of compounds must be in the program
- Parameters and equations must be accurate
- Extrapolation to “new” molecular structures may be dangerous
- Does not deal with electrons

Applications of Molecular Modeling

- Understanding Mechanisms
- Understanding Conformations
- Understanding Biological Activity
- Understanding Protein Structures

Comparison of the Performance of Molecular Mechanics (MM) and Quantum Methods (QM):



Task	MM	Semi-Empirical	Ab initio		DFT
			HF	Correlated	
Geometry	S	S	S	S	S
Transition-state Geometry	-	S	S	S	S
Conformation	S	**U**	S	S	S
Thermochemistry	-	**U**	S	S	S

S= satisfactory; U= unsatisfactory