We showed that for a monatomic gas ($\varepsilon = \varepsilon_{tr}$, $\varepsilon_{int} = 0$) consisting of particles confined to a cubic region of physical space of volume $V$, the permissible quantum energy states are:

$$\varepsilon_{tr} = \frac{h^2}{8mV^{2/3}} \left( n_x^2 + n_y^2 + n_z^2 \right)$$

Here, $n_j$ (j=x,y,z) =1,2,... represent the translational quantum numbers, one for each coordinate that the overall Schrödinger equation is factored into. Note that the energy states can be degenerate (i.e., there can be many combinations of $n_j$ that give rise to the same values of translational energy). Often, we speak of energy levels, and introduce the level degeneracy, $g_{tr}$, as the number of possible combinations of quantum numbers that give rise to the same translational energy. To enumerate these states, we need to know the energy levels, and their degeneracy. Note also that there is a zero-point energy (the translational energy cannot take on the value of zero). A particle with zero energy (or zero momentum) would require an infinite deBroglie wavelength (giving it some probability of being outside the box), which is unphysical, and would violate the imposed boundary condition.

In general, a molecule has internal energy (electronic, vibrational, rotational), as a result of an interatomic potential interaction. For independent modes, the interaction potential energies are separable. Each mode has an associated Schrödinger equation, which gives as eigenvalues the mode energy states. Under these conditions, the total energy $\varepsilon = \varepsilon_{tr} + \varepsilon_{elec} + \varepsilon_{vib} + \varepsilon_{rot}$. Solving the Schrödinger equation for arbitrary atomic or molecular structure is the subject of ongoing research. In this summary, we shall discuss briefly, the results for the electronic structure of hydrogen, and the vibrational and rotational structure of simple molecules (diatomic).

**Electronic States** Even for the simplest of atoms (i.e., atomic hydrogen) the solution of the Schrödinger equation for the electronic wavefunction, is an undertaking. For a single electron system such as atomic hydrogen*, the interaction potential between the positively charged nucleus and the orbiting electron is

$$\phi_{elec} = \frac{e^2}{4\pi\varepsilon_o r}$$

resulting in having to solve:

$$\frac{h^2}{8\pi^2 m_e} \nabla^2 \psi_{elec} + (\varepsilon_{elec} + \frac{e^2}{4\pi\varepsilon_o r})\psi_{elec} = 0$$

In principle, the wave equation is separable using $\psi_{elec} = \psi_{elec_r} \cdot \psi_{elec_\ell} \cdot \psi_{elec_m}$, giving rise to three differential equations, the solution of each giving the radial, azimuthal, and magnetic wave functions, along with the corresponding energies, characterized by the electronic configuration quantum numbers, $n$ (radial or principle), $\ell$ (orbital), and $m$ (magnetic), where:

- $n = 1, 2, \ldots \infty$
- $\ell = 0, 1, 2, \ldots (n-1)$
- $m = 0, \pm 1, \pm 2, \ldots \pm \ell$

* many electron systems (e.g., helium) must also include the interaction between electrons.
(Note that the range of \( \ell \) and \( m \) are related to \( n \)). Finally, there is a fourth quantum number that is associated with the electron spin, \( s = \pm \frac{1}{2} \). Fortunately, for atomic hydrogen, the combinations of \( \ell \), \( m \), and \( s \) quantum numbers having a common principle quantum number \( n \) give rise to energies that are very close together. As a result, we introduce (for hydrogen) the energy levels associated with the principle quantum number \( n \),

\[
\varepsilon_{e_{lec}} = \frac{m_e e^4}{8\hbar^2 \varepsilon_0^2} \left(1 - \frac{1}{n^2}\right)
\]

Note that increasing \( n \) corresponds to an increasing electron orbital radius (in the Bohr model). As \( n \) approaches \( \infty \) (\( r \) approaches \( \infty \)), the energy approaches the ionization energy of hydrogen.

We see that for \( n = 1 \), we have \( \ell = 0, m = 0, s = \pm \frac{1}{2} \), so that there are two (2) possible combinations of quantum numbers for the first energy level \( (n = 1) \) appropriately termed the "ground electronic state" \( g_{elec_1} = 2 \). For \( n = 2 \), we have \( \ell = 0,1; m = 0, \pm 1; \) and \( s = \pm \frac{1}{2} \). We can have then

For \( n = 2 \)
- \( \ell = 0 \): \( m = 0 \) and \( s = \pm \frac{1}{2} \) (2 combinations)
- \( \ell = 1 \): \( m = 0 \) and \( s = \pm \frac{1}{2} \) (2 combinations)
- \( \ell = 1 \): \( m = 1 \) and \( s = \pm \frac{1}{2} \) (2 combinations)
- \( \ell = 1 \): \( m = -1 \) and \( s = \pm \frac{1}{2} \) (2 combinations)

The total number of combinations for \( n = 1 \) is 8 \( (g_{elec_1} = 8) \). In general, we will find that the electronic level degeneracy for hydrogen is \( g_{elec_n} = 2n^2 \). Note also that the energy levels get closer together as the principle quantum number increases. This is often true for most atoms. Only under rare circumstances (i.e., plasmas) is the 2nd or 3rd energy level significantly populated. The electronic structure of other atoms is obviously more complicated than that of hydrogen and will be dealt with on an individual basis. (§IV.11)

**Vibrational and Rotational States of Diatomic Molecules**

For a classical simple harmonic oscillator (SHO) described as two masses \( (m_A, m_B) \) separated by a distance \( r \), bound by an attractive potential of the form \( \phi_{vib} = \frac{1}{2} k_{vib} (r - r_{eq})^2 = \frac{1}{2} k_{vib} x^2 \) (here \( r_{eq} \) is the equilibrium separation), the solution to the classical equation of motion gives rise to the resonance frequency \( v_{vib} = \sqrt{\frac{k_{vib}}{m_{AB}}} \). The amplitude of the vibration, \( A \), can take on arbitrary values depending on the vibrational energy \( A = \sqrt{\frac{2k_{vib} \varepsilon_{vib}}{k_{vib}}} \), because the vibrational energy is continuous, and is a function of the momentum of either particle, \( P \):

\[
\varepsilon_{vib} = \frac{P^2}{2m_{AB}} + \frac{1}{2} k x^2.
\]

While vibrating, the classical SHO can rotate about an arbitrary axis. The rotational energy of the two masses separated by a distance, \( r \), about a common center of mass is:

\[
\varepsilon_{rot} = \frac{1}{2} I \omega^2
\]

where \( I = m_{AB} r^2 \) is the moment of inertia about some axis (related to the angular momentum, \( L \) through \( I = L/\omega \)) and \( \omega \) is the angular velocity of rotation. In principle, the vibrational and rotational motion is coupled, since \( I \) depends on the interatomic separation, and since an additional radial force (centripetal) acts on the vibrating masses due to rotation. In practice, we assume that the energies
are independent and that vibrational motion does not greatly influence the moment of inertia, and visa versa (independent energy modes). In the rigid rotor (RR) approximation, the separation between atoms is assumed to be \( r_{eq} \), effectively decoupling the energy modes.

If we assume that the energy of vibration is independent of the energy of rotation, then the rotational energy becomes:

\[
\varepsilon_{\text{rot}} = \frac{1}{2} I_{eq} \omega^2
\]

where \( I_{eq} = m_{AB} r_{eq}^2 \).

For a harmonic quantum oscillator and quantum rigid rotator, we must solve the Schrödinger equation:

\[
\frac{\hbar^2}{8\pi^2 m_{AB}} \nabla^2 \psi_{\text{rovib}} + \left( \varepsilon_{\text{rovib}} - \frac{1}{2} k_{\text{rovib}} (r - r_{eq}^2) \right) \psi_{\text{rovib}} = 0
\]

Like electronic motion about a nucleus, this problem is best treated in spherical coordinates, in which case the vector operator \( \nabla^2 = \nabla^2_{r,\theta,\phi} \). When the energy of rotation and vibration can be considered to be independent, and when the interaction potential is independent of the coordinates \( \theta,\varphi \), the above equation can be separated using \( \psi_{\text{rovib}} = \psi_{\text{rot}} \psi_{\text{vib}} \) and \( \varepsilon_{\text{rovib}} = \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} \). The corresponding Schrödinger equation describing the vibrational wavefunction and eigenvalue is:

\[
\frac{\hbar^2}{8\pi^2 m_{AB}} \frac{d^2}{dx^2} \psi_{\text{vib}} + \left( \varepsilon_{\text{vib}} - \frac{1}{2} k x^2 \right) \psi_{\text{vib}} = 0
\]

subject to the boundary conditions that:

\[
\psi_{\text{vib}}(x \to \infty) = 0
\]

\[
\frac{d\psi_{\text{vib}}}{dx} = 0 \quad x = 0
\]

Once again, this is an eigenvalue equation, and we see that there is only a set of discrete energies that will satisfy the imposed boundary conditions (eigenvalues). The solution to the quantum oscillator amplitudes and energies can be obtained either numerically or in closed form, the results of which are stated here without proof (§IV. 12 Eq. 12.9a):

\[
\varepsilon_{\text{vib}} = \left( i + \frac{1}{2} \right) \hbar \nu_{\text{vib}}
\]

with the vibrational quantum number \( i = 0, 1, \ldots \). Note that there is a single quantum number, because of the one dimensional motion of the oscillator, and so the degeneracy of the energy levels is \( g_{\text{vib}} = 1 \) (one quantum state /energy level). The zero-point energy is a consequence of the Heisenberg Uncertainty Principle, indicative of the fact that a zero amplitude would have to violate this principle since both the position and energy would be known precisely.

Some characteristic vibrational frequencies \( \nu_{\text{vib}} \) of common diatomic molecules are given below.
Values of the $v_{vib}$ are often expressed in terms of the characteristic vibrational temperatures $\theta_v = h v_{vib} / k$. Characteristic vibrational temperatures are also given in the above table.

Solution for the motion about $\theta, \varphi$ gives (like the electronic states) two additional quantum numbers, $\ell_{rot}$, and $m_{rot}$:

$$\ell_{rot} = 0, 1, 2, \ldots$$
$$m_{rot} = 0, \pm 1, \pm 2, \ldots \pm \ell_{rot}$$

The combinations of $m_{rot}$ having a common quantum number $\ell_{rot}$ (there are $2\ell_{rot} + 1$ values of $m_{rot}$ for each $\ell_{rot}$) give rise to the same energies. As a result, we introduce the energy of the levels associated with rotation (§IV. 12 Eq. 12.1):

$$\varepsilon_{\ell_{rot}, I} = \frac{\ell_{rot} (\ell_{rot} + 1) h^2}{8\pi^2 I}$$

and the rotational energy degeneracy $g_{\ell_{rot}} = 2\ell_{rot} + 1$.

For each vibrational energy state, there is a manifold of rotational states, the separation of which increases approximately with $\ell_{rot}^2$. Note that the lowest rotational energy state is zero. This does not violate the Uncertainty Principle since the molecule in this lowest rotational state is still in motion in accordance with its vibrational state.

It is sometimes convenient to introduce a characteristic rotational temperature $\theta_r = h^2 / 8\pi^2 I k$ which gives the moment of inertia, $I$. The values of $\theta_r$ and $I$ for common diatomic molecules found in high temperature air are given in the table below.

<table>
<thead>
<tr>
<th>molecule</th>
<th>$I \times 10^{-46}$ Kg m$^2$</th>
<th>$\theta_r$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>1.92</td>
<td>2.1</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1.39</td>
<td>2.9</td>
</tr>
<tr>
<td>NO</td>
<td>1.63</td>
<td>2.5</td>
</tr>
</tbody>
</table>