Molecular Electronic Structure

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CONTENTS

I. MOLECULAR STRUCTURE

A. The Born-Oppenheimer approximation

Within the Born-Oppenheimer approximation, the full nuclear-electronic wavefunction $\Psi(\vec{r},\vec{R})$, where $\vec{r}$ refers, collectively to the coordinates of all the elecrons and $\vec{R}$, to the coordinates of all the nuclei, may be expanded in terms of the electronic wavefunctions at a fixed $\vec{R}$, namely

$$\Psi(\vec{r},\vec{R}) = \sum_k C_k(\vec{R})\phi_{el}^{(k)}(\vec{r};\vec{R})$$

where

$$H_{el}(\vec{r};\vec{R})\,\phi_{el}^{(k)}(\vec{r};\vec{R}) = E_{el}^{(k))}(\vec{R})\,\phi_{el}^{(k)}(\vec{r};\vec{R}) \tag{1}$$

and the electronic Hamiltonian is

$$H_{el}(\vec{r};\vec{R}) = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_{i,j}\frac{Z_j}{r_{ij}} + \sum_i\sum_{i'>i}\frac{1}{r_{i,i'}}$$

Here i and i' refer to the electrons and j refers to the nuclei.

At each value of the nuclear coordinates $\vec{R}$ one solves the Schroedinger equation (1) obtaining a complete set of electronic energies and electronic wavefunctions, both of which depend, parametrically, on $\vec{R}$. Then, the Born-Oppenheimer approximation states that the motion of the nuclei is defined by the $C_k(\vec{R})$ expansion coefficients, which satisfy the Schroedinger equation

$$H_{nuc}C_k(\vec{R}) = \mathcal{E}C_k(\vec{R})$$

where

$$H_{nuc} = -\frac{1}{2}\sum_j \frac{\nabla_j^2}{M_j} + E_{(el)}^k(\vec{R}) + \sum_j\sum_{j'>j}\frac{Z_jZ_{j'}}{R_{jj'}}$$

Thus, the potential for the motion of the nuclei is the sum of the electronic energy (which depends on $\vec{R}$) and the nuclear repulsion. The Born-Oppenheimer approximation is discussed in more detail in Appendix B.

In the case of a diatomic molecule, we separate out the motion of the center of mass

$$\vec{\mathcal{R}} = \left[M_1\vec{R}_1 + M_2\vec{R}_2\right]/\left(M_1+M_2\right)$$

from the relative motion

$$\vec{R} = \vec{R}_2 - \vec{R}_1$$

Since the electronic energy and the nuclear repulsion depend only on the relative separation of the two nuclei, not their position in space, the Hamiltonian can be written

$$H_{nuc}(\vec{R}_1, \vec{R}_2) = -\frac{1}{M_1 + M_2}\nabla^2_{\mathcal{R}} - \frac{1}{\mu}\nabla^2_{R} + E^{(k)}_{el}(R) + Z_1 Z_2/R$$

where the reduced mass is defined as $\mu = M_1 M_2/(M_1 + M_2)$. This separation is discussed in more detail in Appendix F.

Since the nuclear Hamiltonian is separable into a sum of terms depending either on $\vec{\mathcal{R}}$ or $\vec{R}$, the nuclear wavefunction can be written as a product

$$C_k(\vec{R}_1, \vec{R}_2) = C_k(\vec{\mathcal{R}}, \vec{R}) = \Phi_k(\vec{\mathcal{R}})\Psi_k(\vec{R}) \quad (2)$$

Here $\Phi_k(\vec{\mathcal{R}})$ is the solution to a particle-in-a-box Hamiltonian, corresponding to the motion of the center-of-mass of the diatomic in a region of constant potential

$$-\frac{1}{2\,(M_1 + M_2)}\nabla^2_{\mathcal{R}}\Phi_k(\vec{\mathcal{R}}) = \mathcal{E}_{n_{\mathcal{X}}, n_{\mathcal{Y}}, n_{\mathcal{Z}}}\Phi_k(\vec{\mathcal{R}})$$

where $n_{\mathcal{X}}$, $n_{\mathcal{Y}}$, and $n_{\mathcal{Z}}$ are the quantum numbers of the particle of mass $M = M_1 + M_2$ in a cubic box.

Also, in Eq. (2) $\Psi_k(\vec{R})$ is the solution of a Schodinger equation for the relative motion of the two nuclei

$$\left[-\frac{1}{2\mu}\nabla^2_{R} + V_{eff}(R)\right]\Psi_k(\vec{R}) = E^{(k)}\Psi_k(\vec{R}) \quad (3)$$

where $V_{eff}(R) = E^{k}_{el}(R) + Z_1 Z_2/R$. Note that the potential depends on the magnitude of the internuclear distance but not its orientation. The solutions of this equation are the vibration-rotation wavefunctions of the diatomic in electronic state k. The total energy is then

$$E_{total} = E^{(k)} + \mathcal{E}_{n_{\mathcal{X}}, n_{\mathcal{Y}}, n_{\mathcal{Z}}}$$

Thus, before one can solve the Schroedinger equation for the motion of the nuclei, one needs the electronic energy as a function of the internuclear coordinates. Just as in the case of atoms, in general, one can not solve the electronic Schroedinger equation for more than one electron. Thus, we need to develop a system of approximations, based on use of the variational principle. Crucial will be the expansion of molecular electronic wavefunctions in terms of Slater determinants based on a product of one electron *molecular* orbitals, which themselves will be expanded as linear combinations of atomic orbitals. To illustrate this LCAO-MO method, we start first with the one-electron hydrogen molecular ion (H_2^+), which has the further advantage that it can be solved exactly.

B. The one-electron H_2^+ ion

The simplest molecule is the one-electron H_2^+ ion, with Hamiltonian

$$H_{el} = -\frac{1}{2}\nabla^2 - 1/r_a - 1/r_b \tag{4}$$

where r_a and r_b is the distance between the electron and the two nuclei. Because the Hamiltonian is cylindrically symmetric, the electronic states of can be characterized by the component of the orbital angular momentum along the molecular axis. The states are designated σ, π, δ, etc. corresponding to $m_l = 0, \pm 1, \pm 2$. Often the projection quantum number is denoted λ.

In the separated atom limit, where $R \to \infty$, the system corresponds to an electron associated with one or the other proton. The two possible states are degenerate, so we can take linear combinations which satisfy the additional symmetry created by the indistinguishability of the two nuclei, namely

$$\lim_{R\to\infty} \phi_{el}^{(\pm)} = N_\pm(R)\,(1s_a \pm 1s_b) \tag{5}$$

where

$$1s_a = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r_a}$$

and similarly for $1s_b$. The "+" and "–" states are usually denoted g and u, respectively. The normalization constant can be obtained by requiring that the wavefunction be normalized, so that

$$
\begin{aligned}
1 = N_\pm^2 \int \phi_{el}^2 \, dV \\
&= N_\pm^2 \int [1s_a + 1s_b]^2 \; dV \\
&= N_\pm^2 \left[\int 1s_a^2 dV + \int 1s_b^2 dV + 2 \int 1s_a 1s_b \, dV \right] \qquad (6)
\end{aligned}
$$

Since the $1s$ functions are normalized, we see that the electronic wavefunctions can be normalized by requiring that

$$N_\pm^2(\vec{r}, R) = \left[\frac{1}{2(1 \pm S(R))} \right]^{1/2} \qquad (7)$$

where the *overlap* is defined as

$$S(R) = \int 1s_a 1s_b \, dV$$

In the united atom limit, where $R = 0$, the $1s_a$ and $1s_b$ functions coincide, and $S = 1$, so that

$$\lim_{R \to 0} \phi_g(\vec{r}) = 1s \qquad (8)$$

as we would expect.

An interesting question is what happens to the u function in the united atom limit ($R \to 0$). You can show (using the expression for $S(R)$ given on the next page) that

$$\lim_{R \to 0} \phi_u(R) \approx \cos\theta \exp(-\zeta r) + \mathcal{O}(R)$$

where r and θ are the usual spherical polar coordinates with origin at the mid-point of the bond. This has the correct angular dependence and radial dependence (at large r) of the $2p_z$ atomic orbital of the united atom, but *not* the correct dependence on r as small r, since $\lim_{r \to 0} 2p_z \sim r \cos\theta \exp(-\zeta r)$.

The variational energy of the g state is

$$E_{el}(R) = \frac{1}{2(1+S)} \left[T_{aa} + T_{bb} + T_{ab} + T_{ba} + V_{aaa} + V_{aab} + V_{bba} + V_{bbb} + V_{aba} + V_{abb} + V_{baa} + V_{bab} \right]$$

where

$$T_{mn} = \int 1s_m \left(-\frac{1}{2} \nabla \right) 1s_m dV$$

and

$$V_{mnk} = \int 1s_m \left(-1/r_k\right) 1s_n dV$$

Not all the T and V terms are independent. By symmetry, you can show that $T_{aa} = T_{bb}$, $T_{ab} = T_{ba}$, $V_{aaa} = V_{bbb}$, $V_{aab} = V_{bba}$, and $V_{aba} = V_{abb} = V_{baa} = V_{bab}$. Thus, the expression for the electronic energy simplifies to

$$\begin{aligned} E_{el}(R) &= \frac{1}{(1+S)} \left[T_{aa} + T_{ab} + V_{aaa} + V_{aab} + 2V_{aba}\right] \\ &= \frac{1}{(1+S)} \left[T_{aa} + V_{aaa} + T_{ab} + 2V_{aba} + V_{aab}\right] \end{aligned} \tag{9}$$

The first two terms correspond to the energy of the H atom (calculated with a $1s$ orbital with exponent ζ, the second two terms correspond to the energy (kinetic + potential) of an overlap density $1s_a 1s_b$, and the last term, to the attraction between an electron on one nucleus and the other nucleus.

All these one-electron integrals can be evaluated. We find

$$S(R) = \left(1 + \rho + \frac{1}{3}\rho^2\right) e^{-\rho}$$

$$V_{aaa} = -\zeta$$

$$V_{aba}(R) = -\zeta(1+\rho)e^{-\rho}$$

$$V_{aab}(R) = -\frac{\zeta}{\rho}\left[1 - (1+\rho)e^{-2\rho}\right]$$

$$T_{aa} = \frac{1}{2}\zeta^2$$

and

$$T_{ab} = -\frac{1}{2}\zeta^2 \left(-1 - \rho + \frac{1}{3}\rho^2\right) e^{-\rho}$$

where $\rho = \zeta R$.

Problem 1 Write a Matlab script to use the expressions immediately above to determine the electronic energy of H_2^+ as a function if the internuclear separation R. Check your expression by knowing that at $\rho = 0$ (the united atom limit) the energy is minimized when $\zeta = 2$ (He^+ ion) and that at $\rho = \infty$ (the separated atom limit) the energy is minimized when $\zeta = 1$ (H atom plus a bare proton). As a further check on your expression, for $\zeta = 1$

at $R = 2$ bohr, the electronic energy is -1.05377 hartree.

Determine the dissociation energy, the equilibrium internuclear separation, and the vibrational frequency if the screening constant is held equal to the value appropriate for the H atom ($\zeta = 1$). Compare these with experiment (see webbook.nist.gov).

Now, at each value of R, you can minimize the energy by varying ζ. Do so, to get the best potential curve for a wavefunction of the form $\phi_{el}^{(+)}$ [$Eq.$ (5)]. Compare the dissociation energy, equilibrium separation, and vibrational frequency with experiment. Finally, use the `contour` command in Matlab to prepare contour plots of the square of the $1\sigma_g$ orbital of H_2^+ for internuclear distances of 1, 2, and 4 bohr. The plots should look similar to Fig. 3, except that the simple $1s_a + 1s_b$ expression does not include polarization of the atomic orbitals.

The Matlab script `h2plus.m` determines the electronic energy of H_2^+ as a function of R with the screening constant held equal to its asymptotic value ($\zeta = 1$). Figure 1 displays the electronic energy resulting from this calculation as well as the effective potential for the motion of the nuclei

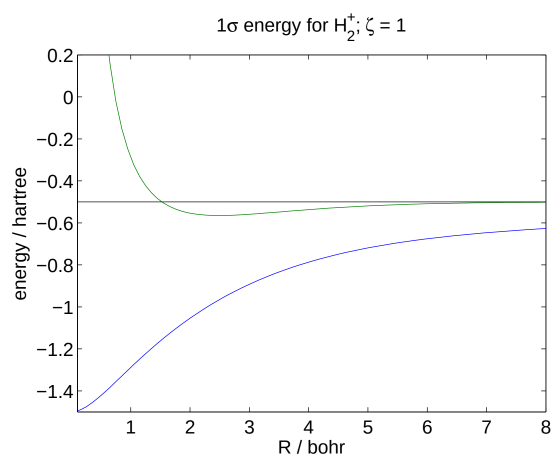

FIG. 1. Electronic energy (blue) and effective nuclear potential (green) for H_2^+ determined from an LCAO-MO wavefunction with $\zeta = 1$.

$$V_{eff}(R) = E_{el}(R) + 1/R$$

as a function of R. We notice two things: (a) The electronic energy goes slowly to zero at long range, because of the long-range attraction between a $1s$ orbital on one atom with the other proton ($V_{aab}(R)$. However, this is cancelled at long range by the proton-proton repulsion ($1/R$) so that at long range the effective potential goes rapidly to zero. Also (b) the depth of the attractive well is quite small in comparison with the large total energies. For this calculation in which we constrain the orbital exponent ζ to equal 1, the dissociation energy is calculated to be $D_e = 0.0648$ hartree $= 1.75$ eV and the position of the minimum is $R_e = 2.046$ bohr.

A better approximation can be obtained by varying allowing the exponent ζ to vary a function of R to minimize the electronic energy. Then, we you add back $1/R$ you obtain a potential which has a dissociation energy of $D_e = 2.35 eV$ at $R_e = 2.003$ bohr.

The true dissociation energy of H_2^+ is 0.1026 hartree $= 2.793$ eV with $R_e = 1.997$ bohr. Why is the simple LCAO-MO wavefunction of Eq. (7) in error? Because we have assumed that the electron is described by a linear combination of spherical orbitals. In fact, the presence of the additional proton will polarize the charge distribution, pulling the electron a bit toward the bare proton. This is shown, schematically, in the next figure

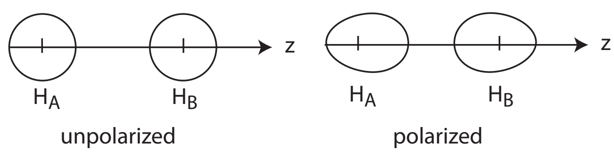

FIG. 2. Illustration of the lowest $1\sigma_g$ orbital of H_2^+. The left cartoon is the primitive linear combination of $1s$ atomic orbitals. The right cartoon shows the effect of polarization of the these atomic orbitals

We could include the effect of polarization by using a more flexible molecular orbital description

$$\phi_g(\vec{r}, R) = C_{1s}\left[\frac{1}{2(1+S_{1s})}\right]^{1/2}(1s_a + 1s_b) + C_{2p}\left[\frac{1}{2(1-S_{2p_z})}\right]^{1/2}(2p_{za} - 2p_{zb}) \qquad (10)$$

where C_{1s} and C_{2p} are variable coefficients. Note the minus sign in the second term. Because of the directionality of the $2p_z$ orbitals, it is the minus linear combination which has g symmetry. Also, because of this directionality, the overlap S_{2p_z} is negative.

C. The H_2 molecule

The electronic Hamiltonian for the two-electron H_2 molecule is

$$H_{el}(1,2) = h(1) + h(2) + 1/r_{12}$$

where $h(1)$ is the one-electron Hamiltonian of Eq. (4). For atoms, the one-electron $1s$ ground state of the H atom provides the logical approximation for the electronic wavefunction of the two-electron He atom, namely $1s^2$. If we follow this approach for H_2 we would write the electronic wavefunction as (using Slater determinantal notation)

$$\phi_{el}(1,2) = |1\sigma_g 1\bar{\sigma}_g| \tag{11}$$

With this choice of a wavefunction, the variational energy is (similar to the case of the He atom)

$$E_{\mathrm{H}_2}(R) = 2\varepsilon_{1\sigma_g} + \left[1\sigma_g^2\middle|\, 1\sigma_g^2\right]$$

One could then invoke the Hartree-Fock approach to determine the best $1\sigma_g$ molecular orbital for H_2, similarly to what we did for the He atom. Figures 3 and 4 show contour and mesh plots of the HF $1\sigma_g$ orbital for H_2 for H_2 at its equilibrium internuclear distance. We see here clearly the evidence of the polarization discussed in connection with the cartoon shown in Fig. 2.

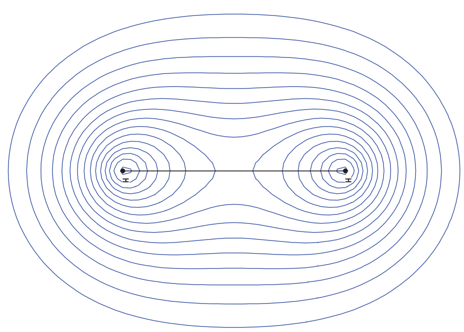

FIG. 3. Contour plot of the lowest $1\sigma_g$ orbital of H_2, for an H–H internuclear separation of 1.4 bohr

Unfortunately, application of the HF approach to molecules is flawed from the very beginning. If we expand the wavefunction of Eq. (11) in terms of the constituent atomic orbitals, we find

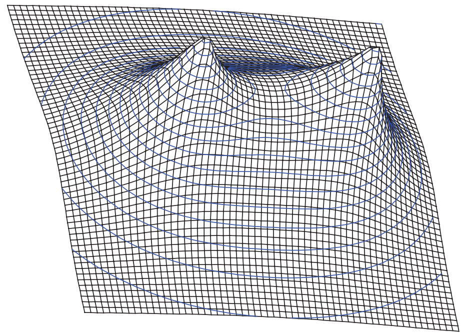

FIG. 4. Surface mesh plot of the lowest $1\sigma_g$ orbital of H_2, for an H–H internuclear separation of 1.4 bohr

$$\phi_{el}(1,2) = \frac{1}{2(1-S^2)}\left[\,|1s_a 1\bar{s}_a| + |1s_b 1\bar{s}_b| + |1s_a 1\bar{s}_b| + |1s_b 1\bar{s}_a|\,\right] \tag{12}$$

The first two determinants correspond to associating both electrons with the same proton, which is an ionic electron configuration, either H^+H^- or H^-H^+, while the later two determinants correspond to the usual covalent description, where each proton contributes one electron to the bond. We know that the ground state pathway for dissociation must lead to the one electron associated with each proton, namely

$$\lim_{R\to\infty} \mathrm{H}_2(R) = \mathrm{H} + \mathrm{H}$$

or, in other words

$$\lim_{R\to\infty} \phi_{el}(1,2) \approx \left[\,|1s_a 1\bar{s}_b| + |1s_b 1\bar{s}_a|\,\right]$$

Thus, a serious flaw of conventional, single-determinant Hartree-Fock calculations on molecules is the inability of a single-determinant wavefunction to describe correctly the dissociation of the molecule.

One way of overcoming this deficiency is to use an approximate wavefunction which does dissociate correctly. This approach was first advocated by Heitler and London. In the HL or "valence-bond" description the ionic configurations in Eq. (12) are eliminated, leaving

$$\phi_{el}(1,2) = \left[\frac{1}{2(1+S^2)}\right]^{1/2}\left[\,|1s_a 1\bar{s}_b| + |1s_b 1\bar{s}_a|\,\right] \tag{13}$$

Since the variational method allows us to introduce increasing flexibility into the wavefunction, while guaranteeing that the energy will always lie above the true ground state electronic energy, we could allow a variable mix of ionic and covalent configurations

$$\phi_{el}(1,2) = C_I \left[\frac{1}{2(1+S^2)}\right]^{1/2} [\,|1s_a 1\bar{s}_a| + |1s_b 1\bar{s}_b|\,] + C_C \left[\frac{1}{2(1+S^2)}\right]^{1/2} [\,|1s_a 1\bar{s}_b| + |1s_b 1\bar{s}_a|\,] \tag{14}$$

where C_I and C_C are variable coefficients which satisfy $C_I^2 + C_C^2 = 1$.

Alternatively, we could write the wavefunction as

$$\phi_{el}(1,2) = C_g\,|1\sigma_g 1\bar{\sigma}_g| + C_u\,|1\sigma_u 1\bar{\sigma}_u| \tag{15}$$

where,

$$\lim_{R\to\infty} 1\sigma_{g(u)} = \left[\frac{1}{2(1\pm S)}\right]^{1/2} (1s_a \pm 1s_b)$$

Note that although the $1\sigma_u$ orbital is antisymmetric with respect to interchange of the two nuclei, the product of two antisymmetric functions is symmetric, so that the $|1\sigma_u 1\bar{\sigma}_u|$ determinant is symmetric, the same as the $|1\sigma_g 1\bar{\sigma}_g|$ determinant.

Thus, a mix of the two determinants in Eq. (15) will allow correct dissociation of the H_2 molecule. One can imagine an extended SCF procedure in which one starts with the two-determinant wavefunction of Eq. (15) [this is called a dual-reference (or, in general, multi-reference) description] and then determines, within a chosen atomic-orbital basis set, the optimal $1\sigma_g$ and $1\sigma_u$ functions and the coefficients C_g and C_u chosen to minimize the electronic energy at each value of R. This is the so-called multi-configuration, self-consistent-field approach (MCSCF).

Figure 5 compares the calculated HF and MCSCF potential energy curves for H_2. The error in the HF method at long range is very visible. Since the single-determinant wavefunction of Eq. (11) is a equal admixture of covalent H_2 and ionic $H{+}H^-$, the asymptotic energy will be the average of the energy of H($1s$)+H($1s$) [$E = -1$ hartree] and H^++H^-($1s$). The energy of the latter is just the sum of the energy of the H atom plus the electron affinity of H (0.277 hartree). As a result, the minimum in the Hartree-Fock curve is substantially too shallow. Table I compares the calculated equilibrium distances and dissociation energies.

Finally, Fig. 6 shows the R dependence of the C_g and C_u expansion coefficients in Eq. (15).

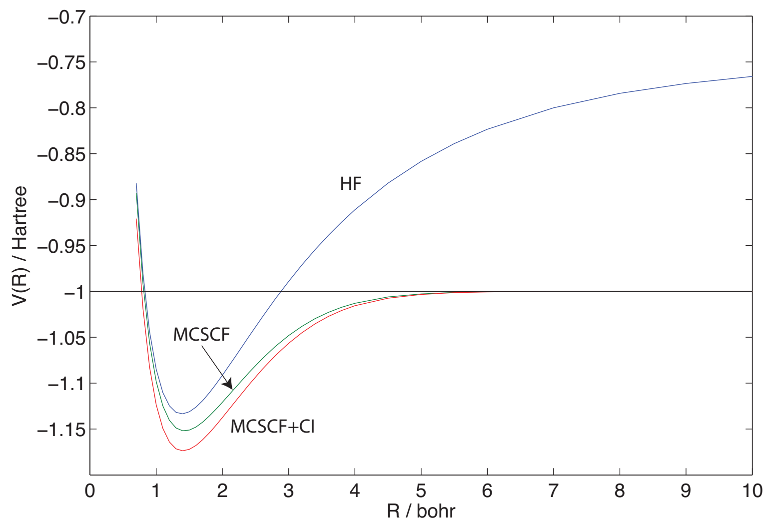

FIG. 5. Calculated potential curves $[V(R) = E_{el}(R) + 1/R]$ for H_2, determined within the single-reference HF method, the two-configuration MCSCF method, and the two-configuration MCSCF method with the addition of configuration interaction.

TABLE I. Calculated internuclear separations and dissociation energies for H_2.

Method	R_e (bohr)	D_e (eV)
HFSCF	1.391	3.638
MCSCF	1.430	4.147
MCSCF+CI	1.407	4.748
exact[a]	1.401	4.747

[a] W. Kolos and L. Wolniewicz, "Potential-Energy Curves for the $X^1\Sigma_g^+$, $b^3\Sigma_u^+$, and $C^1\Pi_u$ States of the Hydrogen Molecule," J. Chem. Phys. **43**, 2429 (1965).

II. HOMONUCLEAR DIATOMICS: FIRST-ROW ELEMENTS

Despite its deficiencies the single-configuration description does provide an excellent description of the electronic wave function for small molecules. As we have seen, the bonding $1\sigma_g$ orbital is singly occupied in H_2^+, but doubly occupied in the H_2 molecule. We would then expect naively that the bond in H_2 would be twice as strong a in the case of the H_2^+ ion. A stronger bond corresponds to a deeper well in the potential $V(R)$. The vibrational motion of a diatomic can be approximated as harmonic motion about the minimum in $V(R)$, with a force constant given by

$$k = \left.\frac{\partial^2 V(R)}{\partial R^2}\right|_{R=R_e}$$

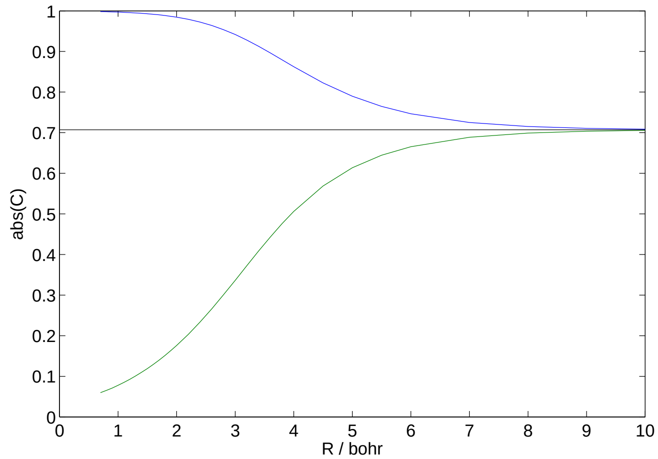

FIG. 6. Calculated coefficients C_g (blue) and C_u (green) in the two-configuration MCSCF approximation to the H_2 electronic wavefunction. The absolute values of the coefficients are shown. The sign of C_u is opposite to that of the sign of C_g.

The vibrational frequency is then

$$\omega = \sqrt{k/\mu}$$

The spacing between adjacent vibrational levels is $\hbar\omega$. Spectroscopists tend to designate this spacing as ω_e in wavenumber units. This value corresponds to $1/\lambda$, where λ is the wavelength of light which corresponds to the vibrational spacing. Thus

$$\omega_e = 1/\lambda = \frac{1}{2\pi c}\sqrt{k\mu}$$

As we have seen, the dissociation energy of H_2 is indeed larger than that of H_2^+, as shown in Table [**?**].

Chemists often describe the strength of a bond in terms of the "bond-order" which is the one-half the total number of electrons in bonding molecular orbitals minus the number of electrons in antibonding molecular orbitals, namely

$$bo = \frac{1}{2}\left(n_{bonding} - n_{antibonding}\right) \tag{16}$$

The depth of the well in $V(R)$ is called D_e (usually defined as a positive number), which is a measure of the strength of the bond. Since the lowest vibrational level of a diatomic molecule – the zero-point energy – is $\hbar\omega/2$, the experimentally-measurable binding energy is less than D_e. This is called D_0, namely

$$D_0 = D_e - \omega_e/2$$

.

Table II lists the values of ω_e, D_0, and R_e for the homonuclear diatomic molecules and ions that can be formed out of the first-row atoms. We observe that the bond energy correlates very well with the bond order. However, going from a bond order of 1/2 to 1 doesn't quite double the binding energy.

TABLE II. States, dominant electronic configurations, and spectroscopic constants for several first-row homonuclear diatomic molecules and ions.

System	Configuration	bo[b]	ω_e[a,c]	D_0[d]	R_e[b,e]
H_2^+	$1\sigma_g^1$	0.5 [f]	2321	2.651	1.052
H_2	$1\sigma_g^2$	1	4401	4.4781	0.7414
He_2^+	$1\sigma_g^2 1\sigma_u^1$	0.5	1698	2.365	1.116
He_2	$1\sigma_g^2 1\sigma_u^2$	0	0	0.090[f]	2.97[f]

.

[a] Bond order, see Eq. (16).
[b] Data from http://webbook.nist.gov.
[c] In wavenumbers.
[d] The dissociation energy out of the lowest vibrational level, in eV, data from K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979)
[e] Distance in Å.
[f] The He_2 molecule shows only a very small van der Walls well at large distance.

III. HOMONUCLEAR DIATOMICS: SECOND-ROW ELEMENTS

Despite the deficiencies of the single-configuration description, the electronic wavefunctions of the larger homonuclear diatomics are built up by assigning electrons to the linear combination of the molecular orbitals built up out of the g and u linear combinations of the orbitals of the atoms. In order of increasing energy, these are listed in Table II.

There are three possible linear combinations of $2p$ atomic orbitals: $2p_{a,m_l=0} \pm 2p_{b,m_l=0}$ and

TABLE III. Molecular orbitals for homonuclear diatomics

MO	LCAO description	b/a[a]
$1\sigma_g$	$1s_a + 1s_b$	b
$1\sigma_u$	$1s_a - 1s_b$	a
$2\sigma_g$	$2s_a + 2s_b$	b
$2\sigma_u$	$2s_a - 2s_b$	a
$3\sigma_g$	$2p_{za} - 2p_{zb}$	b
$1\pi_u$[b]	$2p_{xa} + 2p_{xb}$	b
$1\pi_g$[b]	$2p_{xa} - 2p_{xb}$	a
$3\sigma_u$	$2p_{za} - 2p_{zb}$	a

[a] Each linear combination should be normalized by multiplying by $(1 \pm S)^{-1/2}$ where S is the overlap between the constituent atomic orbitals. The orbitals are described as "bonding" (b) or "antibonding" (a) depending on whether they introduce a buildup of electron probability or a node between the nuclei.
[b] The π orbitals are doubly degenerate.

$2p_{a,m_l=\pm1} \pm 2p_{b,m_l=\pm1}$ In the first case, the atomic and molecular orbitals are cylindrically symmetric with respect to the molecular axis, hence they are labelled σ. In the second case the projection of the electronic orbital angular momentum along the molecular axis is ± 1, so the molecular orbitals are designated π. Note that the g and u label describes the behavior of the orbital under inversion of the electronic coordinates $x \to -x$, $y \to -y$, $z \to -z$. The correspondence between the g and u labels and the + or – signs in the description of the molecular orbital follows from the geometry of the diatomic system, illustrated schematically in Fig. 7. Earlier in this paragraph, we wrote the doubly-degenerate π orbitals as $\pi_{\pm1}$ which

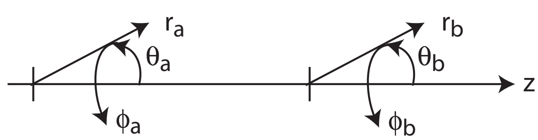

FIG. 7. Coordinate system for a diatomic molecule, consisting of two spherical polar coordinate systems $\{r_a, \theta_a, \phi_a\}$ and $\{r_b, \theta_b, \phi_b\}$, centered on two separate nuclei but both sharing a common z axis.

are eigenfunctions of the z-component of the orbital angular momentum operator $\vec{l}_z$. Equivalently, one can take linear combinations of the $\pi_{\pm1}$ molecular orbitals to form Cartesian orbitals π_x and π_y which are eigenfunctions of the operator for reflection in either the $\{x, z\}$

or the $\{y, z\}$ plane.

A. The diatomic boron molecule

1. $^1\Sigma_g^+$ *state*

The boron atom has 5 electrons, so that the B_2 molecule has 10 electrons. The simplest description of the electronic state of B_2 is $\left|1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2\right|$. As with molecular hydrogen, for proper dissociation, we need a MCSCF description, including the antibonding orbital, namely (where we have dropped the $1\sigma_g$, $1\sigma_u$, and $2\sigma_g$ orbitals to save space)

$$\phi_{el}^{(B)} = C_g \left|\ldots 2\sigma_u^2 3\sigma_g^2\right| + C_u \left|\ldots 2\sigma_u^2 3\sigma_u^2\right|$$

The minimum in the calculated B_2 potential energy curves lies at $R \approx 3.7$ bohr. At this value of R, the orbital energies are given in Table IV.

TABLE IV. Molecular orbital energies for the $^1\Sigma_g^+$ state of B_2, R=3.7 bohr.

Orbital	energy
$1\sigma_g$	-0.763
$1\sigma_u$	-0.757
$2\sigma_g$	-0.557
$2\sigma_u$	-0.448
$3\sigma_g$	-0.427

Figures 8, 9, and 10 show contour plots of the B_2 molecular orbitals at $R = 3.7$ bohr.

Spectroscopists label the electronic state of a diatomic molecule by the total spin multiplicity $2S+1$, the value of the projection of the total electronic orbital angular momentum along the z-axis

$$M_L = \sum_i m_{l_i} ,$$

the total g/u symmetry (if the molecule is homonuclear), and, finally, the symmetry of the electronic wavefunction when the coordinates of all the electrons are reflected in a plane containing the internuclear axis (either the xz or yz plane). The notation is $^{2S+1}\Lambda_{g/u}^{+/-}$, where $\Lambda \equiv \Sigma$ for $M_z = 0$, $\Lambda \equiv \Pi$ for $M_z = \pm 1$, and $\Lambda \equiv \Delta$ for $M_z = \pm$. In the case

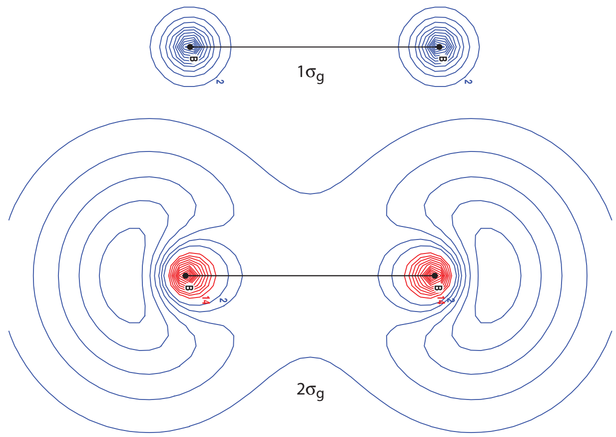

FIG. 8. Contour plot of the $1\sigma_g$ and $2\sigma_g$ orbitals of the B_2 molecule at R=3.7 bohr.

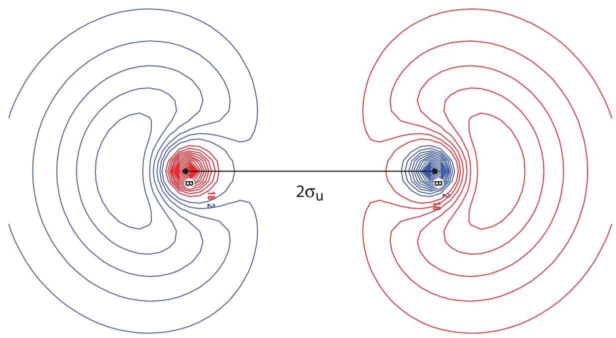

FIG. 9. Contour plot of the $2\sigma_u$ orbital of the B_2 molecule at R=3.7 bohr.

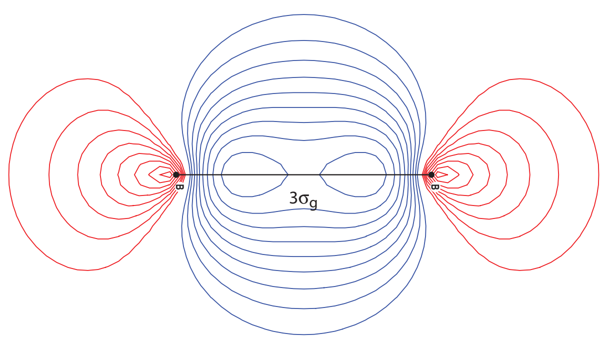

FIG. 10. Contour plot of the $3\sigma_g$ orbital of the B_2 molecule at R=3.7 bohr.

of the electronic state of B_2 discussed in this subsection, the total spin is 0 (since all the molecular orbitals are doubly filled), the projection of the total angular momentum is zero, since all the molecular orbitals are σ orbitals, the g/u symmetry is g (again, since all the molecular orbitals are doubly filled!). Finally, again since all the molecular orbitals occupied are cylindrically symmetric and since all the orbitals are doubly filled, the electronic state has positive symmetry with respect to reflection. Thus the state is a ${}^1\Sigma_g^+$ state.

States with $M_L > 0$ always come in degenerate pairs (± 1, ± 2, etc.). Consider the symmetry with respect to reflection in the xz plane. Let the operator for this operation by called σ_{xz}. For this operation $\phi \rightarrow -\phi$. Since the dependence on ϕ of the $Y_{l=1,m\pm 1}$ spherical harmonics is (http://en.wikipedia.org/wiki/Table_of_spherical_harmonics) is $Y_{1,\pm 1} \sim \mp \exp(\pm i\phi)$, we have, for a single π orbital (regardless of whether it is g or u)

$$\sigma_{xz}\pi_1 = -\pi_{-1} \tag{17}$$

and

$$\sigma_{xz}\pi_{-1} = -\pi_1 \tag{18}$$

If we take linear combinations of these functions,

$$\pi_\pm = 2^{-1/2}\left(\pi_1 \pm \pi_{-1}\right)$$

one will be symmetric and the other, antisymmetric, with respect to reflection in the xz plane. Note that these linear combinations correspond to what one might call Cartesian π orbitals, which we alluded to at the end of the preceding section, namely

$$\pi_x = -2^{-1/2}\left(\pi_1 - \pi_{-1}\right)$$

and

$$\pi_y = 2^{-1/2}\left(\pi_1 + \pi_{-1}\right)$$

You can show, similarly, that for a Slater determinant with any arbitrary number of π orbtials, for the degenerate pair of states with $M_L > 0$ one is symmetric, and the other, antisymmetric, with respect to reflection in any plane containing the z axis. Thus, in the case of Π, Δ, etc. states it doesn't make sense to add the $\pm$ label to the electronic states.

In the case of B_2 in the ${}^1\Sigma_g^+$ state, the bond order is (6-4)/2 = 1, so that the B_2 molecule in this state has a single bond.

2. $^3\Sigma_g^-$ *state*

What makes chemistry interesting is that it is difficult to predict the relative energy spacing of the lowest states of molecules, except when all the shells are filled. As an example, suppose we consider that state of the B_2 molecule with electron occupancy (electronic configuration) $\ldots 2\sigma_u^2 1\pi_u^2$. Because there are two degenerate $1\pi_u$ orbitals, one can construct various different states. Suppose, we put the two outer electrons one in the $1\pi_{u,1}$ and the other in the $1\pi_{u,-1}$ orbital. One possible Slater determinantal wavefunction for this state is

$$\left|{}^3\Sigma_g\right\rangle = |\ldots 1\pi_{u1}1\pi_{u,-1}| \tag{19}$$

here we have explicitly described only the two electrons in the $1\pi_u$ molecular orbital. We use the notation $^3\Sigma_{M_S}$, where M_S is the total projection quantum numbers of the electronic spin angular momenta. Here, we have $M_S = 1$. We could generate the Slater determinants for the two states with $M_S = 0$ and $M_S = -1$ by applying the spin lowering operator $S_- = s_{1-} + s_{2-}$.

Figure 11 shows a contour plot of the B_2 $1\pi_u$ molecular orbital, for $R = 3.3$ bohr, which is the minimum for the $^3\Sigma$ state. Note that the proper spectroscopic designation of this

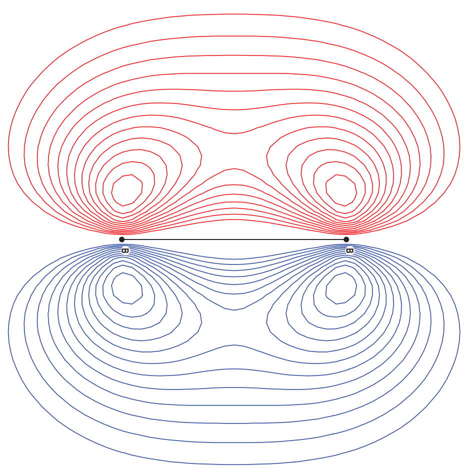

FIG. 11. Contour plot of the $1\pi_u$ orbital of the B_2 molecule in its $^3\Sigma_g^-$ state at R=3.3 bohr.

$|\ldots 1\pi_{u1}1\pi_{u,-1}|$ state is $^3\Sigma_g^-$. The state is g, because every orbital of u symmetry ($1\sigma_u$, $2\sigma_u$, $1\pi_u$) is doubly occupied. However, the state is "–" symmetry with respect to reflection because, from Eqs. (17) and (18)

$$\begin{aligned}\sigma_{xz}\left|{}^3\Sigma_g\right\rangle &= (\sigma_{1,xz}\sigma_{2,xz})\,|\ldots 1\pi_{u1}1\pi_{u,-1}| \\ &= |\ldots(-1\pi_{u,-1})(-1\pi_{u,1})| \\ &= |\ldots 1\pi_{u,-1}1\pi_{u,1}| = -\,|\ldots 1\pi_{u,1}1\pi_{u,-1}| \\ &= -\left|{}^3\Sigma_g^-\right\rangle \end{aligned} \tag{20}$$

In fact, the energy of the ${}^3\Sigma_g^-$ state at its minimum is 0.73 eV *below* the energy of the ${}^1\Sigma_g^+$ state at its minimum. Although both states have a bond order of 1, the ${}^3\Sigma_g^-$ state lies a bit lower because electron repulsion in a triplet state is smaller than in a singlet state.

B. The diatomic oxygen and carbon molecules in their lowest states

1. O_2

The lowest electronic states of C_2 and O_2 offer an interesting study in the subtleties of electronic structure. The latter molecule is actually simpler. The nominal electron occupancy for O_2 is $|1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2|$, with a bond order of 2. Because the $1\pi_g$ orbital is doubly degenerate, but only doubly occupied, we can have various electronic states depending on how we place the electrons. We can use a simplied tableau method (like we used to determine the electronic sates of the C atom; see Table II and III of Chap. 3). We use the tableau to keep track of all the possible assignments of two electrons in two π orbitals with electronic orbital projection quantum numbers of $+1$ and -1, subject to the constraint that no spin-orbital may be doubly occupied.

Since there is only one entry for $M_S = 1$, in the $M_L = 0$ box, there will be a state with $S = 1$ and with a total projection of the electronic orbital angular momentum $M_L = 0$. This we denote as a ${}^3\Sigma$ state. The determinant corresponding to the $M_S = -1$ component of this state occurs in the $M_L = 0$, $M_S = -1$ box. The determinant corresponding to the $M_S = 0$ component of this state can be determined by operating on the $M_S = 1$, $M_L = 0$ state by $S_- = s_{1-} + s_{2-}$, giving

$$\begin{aligned}\left|{}^3\Sigma,\, M_S = 0\right\rangle &= 2^{-1/2}\,[\,|\bar\pi_1\pi_{-1}| + |\pi_1\bar\pi_{-1}|\,] \\ &= 2^{-1/2}\,[\,|\pi_1\bar\pi_{-1}| - |\pi_{-1}\bar\pi_1|\,]\end{aligned} \tag{21}$$

TABLE V. Application of the tableau method to the two $1\pi_g$ electrons in the $|\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g^2|$ state of the O_2 molecule.[a]

$M_S\backslash M_L$	2	0	−2
1		$\pi_1\pi_{-1}$	
0	$\pi_1\bar{\pi}_1$	$\pi_1\bar{\pi}_{-1},\ \pi_{-1}\bar{\pi}_1$	$\pi_1\bar{\pi}_{-1}$
-1		$\bar{\pi}_1\bar{\pi}_{-1}$	

[a] For simplicity we have not indicated the principal quantum number label of the molecular orbitals (here, "1"). Also, here both of the π orbitals have g interchange symmetry, thus the electronic state has g inversion symmetry.

We see that there is one entry each in the $M_L = \pm 2$, $M_S = 0$ boxes. This will correspond to a state with $|M_L = 2|$, $M_S = 0$, a $^1\Delta$ state. Finally, since there are two entries in the $M_S = 0$, $M_L = 0$ box, but only one entry in every other box, it follows that there will be another state with $M_L = M_S = 0$. There are no other unaccounted for components. Note that you can't use L_- to go from one M_L box to another. This is because L is not a good quantum number when the spherical symmetry is lifted. Thus, the remaining state in the tableau has $S = 0$ and $|M_L| = 0$. This is a $^1\Sigma$ state. The wavefunction for this state has to be orthogonal to the other state with $M_L = M_S = 0$ which is given in Eq. (21). Consequently,

$$\begin{aligned} \left|{}^1\Sigma,\ M_S = 0\right\rangle &= 2^{-1/2}\left[\, |\bar{\pi}_1\pi_{-1}| - |\pi_1\bar{\pi}_{-1}|\,\right] \\ &= 2^{-1/2}\left[\, |\pi_1\bar{\pi}_{-1}| + |\pi_{-1}\bar{\pi}_1|\,\right] \end{aligned} \tag{22}$$

2. *Reflection symmetry*

The definite-m $p_{\pm 1}$ orbitals are linear combination of the Cartesian p_x and p_y orbitals [Eq. (63) of Chap. 2]. Thus it is easy to show that reflection in the xz plane, where the molecular axis lies along z, obeys the relation

$$\sigma_{xz}\left|{}^3\Sigma,\ M_S\right\rangle = -\left|{}^3\Sigma,\ M_S\right\rangle$$

for all three values of M_S. , and is hence labelled a $^3\Sigma_g^-$ state. Here we have added the g/u symmetry label. Also, as discussed above in Sec. III A 2, a $^3\Sigma$ state originating from a π^2

electron occupancy has "–" reflection symmetry. Similarly, the $^1\Sigma$ state has "+" reflection symmetry – a $^1\Sigma_g^+$ state.

The two components of the Δ state have the reflection symmetry

$$\sigma_{xz} \left| {}^1\Delta_{M_L=\pm1} \right\rangle = \left| {}^1\Delta_{M_L=\mp1} \right\rangle$$

Thus we can take linear combinations of the two definite-m $^1\Delta$ states to give two states of definite reflection symmetry

$$\left| {}^1\Delta_g^+ \right\rangle = 2^{-1/2} \left[\, |\pi_x\bar{\pi}_x| - |\pi_y\bar{\pi}_y| \, \right]$$

and

$$\left| {}^1\Delta_g^- \right\rangle = 2^{-1/2} \left[\, |\pi_x\bar{\pi}_y| + |\pi_y\bar{\pi}_x| \, \right]$$

These states are also labelled $\Delta_{x^2-y^2}$ and Δ_{xy}, for obvious reasons. In general, there exist both a "–" and "+" component for each state with $|M_L| \neq 0$. Hence, the $\pm$ reflection symmetry label is added only to states of Σ cylindrical symmetry.

It is easy to show that for all three M_S components of the $^3\Sigma$ state

$$\sigma_{xz} \left| {}^3\Sigma \, M_S = 1, 0, -1 \right\rangle = - \left| {}^3\Sigma \, M_S = 1, 0, -1 \right\rangle$$

Hence, the $^3\Sigma$ state has "–" reflection symmetry. In terms of Cartesian orbitals, the wavefunctions for the three components of the $^3\Sigma$ state are

$$\left| {}^3\Sigma, \, M_S = 1 \right\rangle = |\pi_x\pi_y|$$

$$\left| {}^3\Sigma, \, M_S = -1 \right\rangle = |\bar{\pi}_x\bar{\pi}_y|$$

$$\left| {}^3\Sigma, \, M_S = 0 \right\rangle = 2^{-1/2} \left[\, |\pi_x\bar{\pi}_y| - |\pi_y\bar{\pi}_x| \, \right]$$

Similarly, you can show that the reflection symmetry of the $^1\Sigma$ state, whose wavefunction is given in Eq. (22), is

$$\sigma_{xz} \left| {}^1\Sigma, \, M_S = 0 \right\rangle = \left| {}^1\Sigma, \, M_S = 0 \right\rangle$$

In terms of Cartesian orbitals, the wavefunction for the ${}^1\Sigma_g^+$ state is

$$\left|{}^1\Sigma_g^+\right\rangle = 2^{-1/2}\,[\,|\pi_x\bar{\pi}_x| + |\pi_y\bar{\pi}_y|\,]$$

3. Electron repulsion

Just as in our study of the carbon atom, the splitting between the electronic energy of the valence states of O_2 is governed by the differences in the average value of the electron repulsion in these states. We need concentrate only on the partially filled $1\pi_g$ subshell, since everything else is doubly occupied, independently of how the $1\pi_g$ subshell is filled. Following our analysis in Chap. 3 and using the results in Appendix A for expectation values of two-electron operators between Slater determinantal wavefunctions, we find that the average value of $1/r_{12}$ between the two π_g electrons in O_2 is

$$\langle 1/r_{12}\rangle_{{}^3\Sigma_g^-} = \left[\pi_x^2\middle|\,\pi_y^2\right] - [\pi_x\pi_y|\,\pi_y\pi_x]$$

$$\langle 1/r_{12}\rangle_{{}^1\Sigma_g^+} = \left[\pi_x^2\middle|\,\pi_x^2\right] + [\pi_x\pi_y|\,\pi_y\pi_x]$$

$$\langle 1/r_{12}\rangle_{{}^1\Delta_g^+} = \left[\pi_x^2\middle|\,\pi_x^2\right] - [\pi_x\pi_y|\,\pi_y\pi_x]$$

and

$$\langle 1/r_{12}\rangle_{{}^1\Delta_g^-} = \left[\pi_x^2\middle|\,\pi_y^2\right] + [\pi_x\pi_y|\,\pi_y\pi_x]$$

Since the energies of the two components of the ${}^1\Delta$ states must be identical, equating the last two equations gives

$$\left[\pi_x^2\middle|\,\pi_x^2\right] = \left[\pi_x^2\middle|\,\pi_y^2\right] + 2\,[\pi_x\pi_y|\,\pi_y\pi_x]$$

Thus, the ${}^3\Sigma^-$ state will lie lowest in energy. The ${}^1\Delta$ state will lie above, separated by twice the exchange integral $[\pi_x\pi_y|\,\pi_y\pi_x]$. Finally, the ${}^1\Sigma^+$ state will lie above the ${}^1\Delta$ state, separated by, again, twice the exchange integral. The predicted splitting is then, in units of this exchange integral, ${}^1\Delta_g -{}^3\Sigma_g^- = 1$ and ${}^1\Sigma_g^+ -{}^1\Delta_g = 1$.

4. MCSCF calculations for O_2

Because the wavefunction for the $^1\Sigma$ state can't be represented by a single determinant, it is not possible to carry out a conventional HF-SCF calculation for all three states of O_2. However, it is possible to carry out an MCSCF calculation in which we include both the three bonding ($3\sigma_g$, $1\pi_{ux}$, and $1\pi_{uy}$) as well as the three antibonding ($3\sigma_u$, $1\pi_{gx}$, and $1\pi_{gy}$) orbitals. The resulting potential curves are shown in in the left panel of Fig. 12. We see

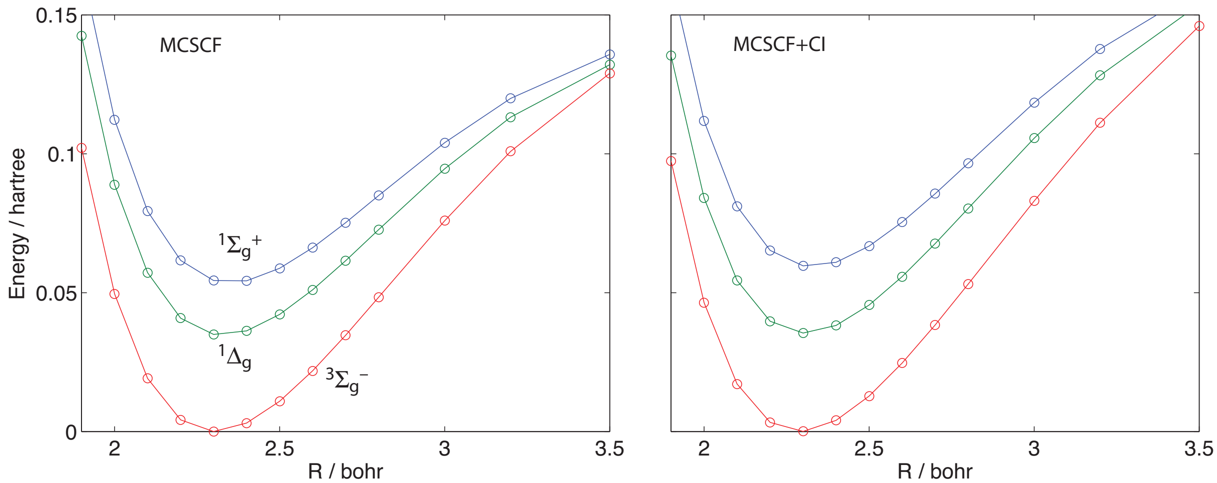

FIG. 12. Electronic potential curves for O_2 determined with complete-active-space (CAS) SCF calculations (left panel) and with CASSCF+CI calculations (right panel).

that the anticipated $^3\Sigma_g^- <^1 \Delta_g <^1 \Sigma_g^+$ ordering is found.

The spacing is not quite the identical spacing predicted in the preceding subsection. This is likely a consequence of the slightly better description, in any approximate calculation, of the triplet state, because the electrons are automatically kept away from each other in a triplet state. By carrying out a configuration-interaction calculation after the CAS-SCF step, we can describe better the so-called "dynamical" correlation. The right panel of Fig. 12 shows the potential curves predicted by CAS-SCF-CI calculations with a larger basis set. We see that the relative spacing of the three curves come closer to the predicted 1:1 ratio.

Because the first electronic excitation in O_2 will involve excitation of an electron from the antibonding $1\pi_g$ orbital to the $3\sigma_u$ orbital, which lies significantly higher in energy, there will likely be no excited states of O_2 except deep into the ultraviolet. The transition between the $^1\Delta_g$ and $^1\Sigma_g^+$ states occurs in the green region of the spectrum, but this transition is not dipole allowed and is hence very week.

5. The C_2 molecule

The situation in the C_2 molecule is more complicated. There are 12 electrons. Once the $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, and $2\sigma_u$ orbitals are filled, that leaves 4 electrons to distribute among the 3 bonding molecular orbitals $3\sigma_g$, $1\pi_{ux}$ and $1\pi_{uy}$. One possible assignment is $|\ldots 3\sigma_g^2 1\pi_u^2|$, which will give rise to the same ${}^1\Sigma_g^+$, ${}^1\Delta$ and ${}^3\Sigma_g^-$ states as in the case of O_2. Another assignment is $|\ldots 3\sigma_g^1 \pi_u^3|$. This will give rise to singlet and triplet Π_u states. These Π states have odd ("u") inversion symmetry because the $1\pi_u$ orbital is triply filled. In addition, there is the third possible assignment $|\ldots 3\sigma_g^0 \pi_u^4|$. This will give rise to only a ${}^1\Sigma_g^+$ state.

Problem 2 Follow the discussion in subsubsection III B 1, and use the tableau method to determine Slater determinantal wavefunctions for the allowed states of C_2 with electron occupancy $|\ldots 3\sigma_g^2 1\pi_u^2|$, $|\ldots 3\sigma_g^1 1\pi_u^3|$, and $|\ldots 3\sigma_g^0 1\pi_u^4|$. In each case, label the wavefunction by the multiplicity $2S+1$, and the value of $\Lambda\,(\Sigma, \Pi, \Delta)$ as well as the g/u symmetry.

The left panel of figure 13 shows the dependence on R of the potential energy curves for the lowest ${}^1\Sigma_g^+$, ${}^1\Delta_g$, ${}^3\Sigma_g^-$ and ${}^{1,3}\Pi_u$ states of C_2. We observe that the ${}^1\Sigma_g^+$ state has a

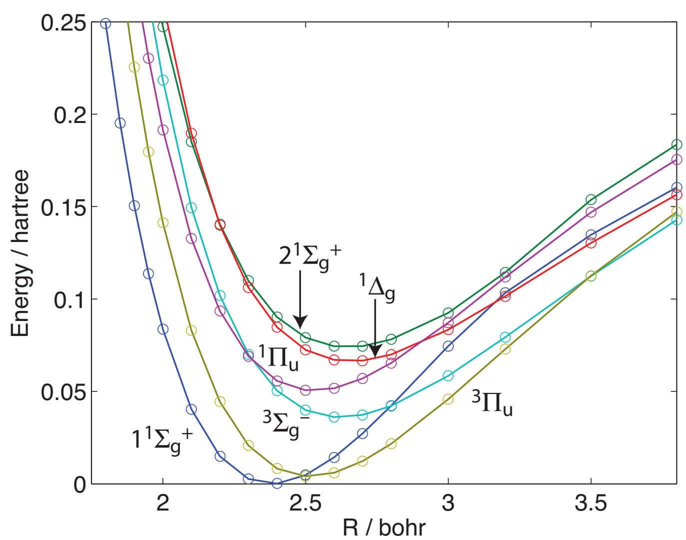

FIG. 13. Electronic potential curves for C_2 determined with complete-active-space (CAS) SCF calculations.

slightly lower potential curve than the triplet state. This is contrary to what one might have expected, since triplet states are usually lower in energy. Why is this? Because, as discussed above, here there is an additional electronic occupancy possible only for a $^1\Sigma$ state, namely $|\ldots 2\sigma_u^2 3\sigma_g^0 \pi_u^4|$. In addition, there is a third possible electron occupancy which involves promoting the antibonding $2\sigma_u$ orbital, namely $|\ldots 2\sigma_u^0 3\sigma_g^2 1\pi_u^4|$, which has a bond order of 3. Both of these electron occupancies are not possible for a state with triplet multiplicity or with $\Lambda \neq 0$. The additional flexibility introduced by these two additional configurations help lower the energy of the $^1\Sigma_g^+$. state. We can write the wavefunction of the $^1\Sigma_g^+$ state of C_2 as

$$\left|{}^1\Sigma_g^+\right\rangle = C_1\left|\ldots 2\sigma_g^2 2\sigma_u^2 3\sigma_g^0 1\pi_u^4\right| + C_2\left|\ldots 2\sigma_g^2 2\sigma_u^0 3\sigma_g^2 1\pi_u^4\right| \\ + C_3 2^{-1/2}\left[\left|\ldots 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_{ux}^2\right| + \left|\ldots 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_{uy}^2\right|\right] + \ldots \quad (23)$$

Figure 14 shows the variation with R of the squares of the C_1, C_2, and C_3 expansion coefficients. We see that in the region of the minimum in the potential energy curve for the

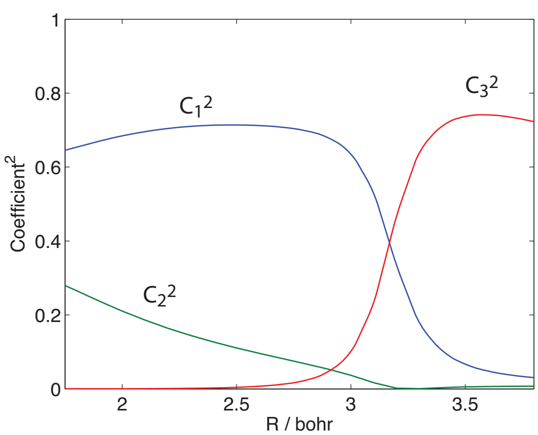

FIG. 14. Variation with distance of the square of the larger coefficients in the expansion of the wavefunction [see Eq. (23)] for the $^1\Sigma_g^+$ state of C_2 determined with complete-active-space (CAS) SCF calculations.

$^1\Sigma_g^+$ state ($R \approx 2.4$ bohr), both the $\ldots 2\sigma_g^2 2\sigma_u^2 3\sigma_g^0 1\pi_u^4$ and $\ldots 2\sigma_g^2 3\sigma_g^2 1\pi_u^4$ occupancies make a substantial contribution to the electronic wavefunction. Only at larger distances does the $\ldots 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^2$ occupancy play a role. We say, then, that the ground state of C_2 illustrates significant "multireference" character. Because the $\ldots 2\sigma_u^0 3\sigma_g^2 1\pi_u^4$ configuration, which has a bond order of 3, makes a significant contribution to the lowest $^1\Sigma_g^+$ state, the minimum in the potential energy curve of the $^1\Sigma_g^+$ state (Fig. 13) lies at a smaller value of R than the minima in the other states, for which the electronic wavefunctions have bond orders of 2.

Since the lowest ${}^1\Sigma^+$ state is predominately $3\sigma_g^0 1\pi_u^4$ at shorter distance but predominately $3\sigma_g^2 1\pi_u^2$ at larger distance, we can say that the $1\pi_u$ orbital lies lower in energy at shorter distances (and hence is filled before the $3\sigma_g$ orbital). At larger distances, this situation is reversed, so that the $3\sigma_g$ orbital is filled first. Figure 15 shows the dependence on R of the energies of the $3\sigma_g$ and $1\pi_u$ orbitals. We observe that the relative energies do reverse, although not exactly at the point where we observe in Fig. 14 the reversal of the relative contributions of the $\ldots 2\sigma_g^2 2\sigma_u^2 3\sigma_g^0 1\pi_u^4$ and $\ldots 2\sigma_g^2 3\sigma_g^2 1\pi_u^4$ occupancies.

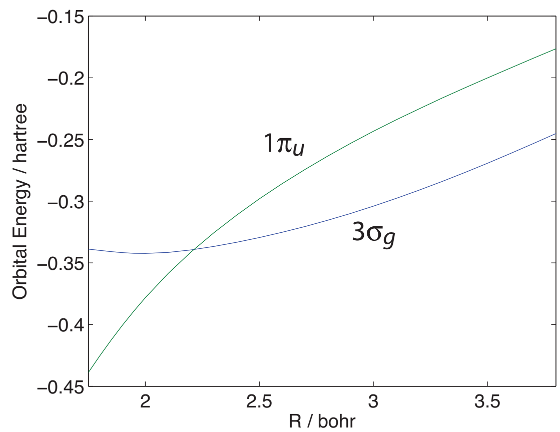

FIG. 15. Variation with distance of the energies of the $3\sigma_g$ and $1\pi_u$ orbitals of C_2 determined from complete-active-space (CAS) SCF calculations.

The lowest vibrational level of the ${}^3\Pi_u$ state lies only $\approx$ 600 cm^{-1} above the lowest vibrational level of the ${}^1\Sigma_g^+$ state. At thermal equilibrium, the population of any electronic state $|j\rangle$ will be $p_j = g_j \exp(-E_j/k_B T)$, where g_j is the degeneracy of the state, E_j is the energy of the state (relative to the ground state), and k_B is Boltzmann's constant. Because the degeneracy of a triplet Π state is 6 (three spin projections multiplied by two values of Λ), but that of a ${}^1\Sigma$ state is only 1, at moderate temperature the ${}^3\Pi$ state of C_2, even though it lies at slightly higher energy, will be significantly populated. This is one of the rare occurrences where two electronic states compete for population even at low temperature.

The lowest triplet state of C_2 corresponds to the electron occupancy $\ldots 2\sigma_u^2 3\sigma_g^1 1\pi_u^3$. The first excited triplet state (${}^3\Sigma_g^-$) corresponds to the $\ldots 2\sigma_u^2 3\sigma_g^2 1\pi_u^2$ electron occupancy. As we discussed in our study of the B_2 and O_2 molecules, the triplet coupled arrangement of the spins in a π^2 configuration gives rise to a ${}^3\Sigma^-$ state. Here, this state also has a bond order of 2, and hence lies not much above the ground triplet state. Thus electronic transitions from the lowest triplet ($^3\Pi_u$) to the $^3\Sigma_g^-$ state lie in the visible region of the spectrum. They are called the "Swann" bands, and are characteristic of the spectra of burning hydrocarbons – they are the blue color in the flame of a gas stove or in a Bunsen burner.

Problem 3 The data file C2_MRCIQ_energies.txt lists, in the region of the molecular minimum, calculated values of $V(R)$ for the $^1\Sigma_g^+$ and the $^3\Pi_g$ states of C_2. Use this data to determine the values of R_e and ω_e (the vibrational frequency, in cm^{-1}) as well as T_0, the splitting between the $v = 0$ vibrational levels of these two electronic states. Compare these results with experiment Then, plot the relative Boltzmann populations of these two states as a function of temperature over the range 200–2000 K.

C. Spectroscopic notation for diatomic molecules

Traditionally, spectroscopists label each electronic state by a letter, as well as the $^{2S+1}\Lambda^{\pm}_{g/u}$ lebel. The lowest state is labelled X. The excited states are then labelled alphabetically, starting with A. Upper case letters are used for states with the same multiplicity as the ground state, while lower case letters are used for states with a different multiplicity. Thus, for O_2, the lowest state is the $X\,^3\Sigma_g^-$ state, followed, in terms of increasing energy, by the $a\,^1\Delta_g$ and the $b\,^1\Sigma_g^+$ states. For C_2, the lowest state is the $X\ ^1\Sigma_g^+$, followed by the $a\,^3\Pi_u$, $b\,^3\Sigma_g^-$ and then the $A\,^1\Pi_u$ state. Occasionally, new states are found which lie in between previously assigned states; these states are labelled A' or B'.

For molecular nitrogen (and molecular nitrogen only) the upper/lower case naming scheme is reversed: The ground state is an $^1\Sigma_g^+$ state (corresponding to the electron occupancy $|\ldots 2\sigma_u^2 3\sigma_g^2 1\pi_u^4|$) and is called the X state. However, the excited singlet states (which have the same multiplicity as the ground state) are labelled with *lower*-case letters but all the triplet states are labelled with *upper-case* letters.

D. States of other homonuclear diatomic molecules and ions

Table VI shows the dominant electronic configurations and spectroscopic constants for the ground state and some of the lower excited states of various homonuclear diatomic molecules and ions. We observe the correlation between bond order and the vibrational frequency and internuclear distance. The higher the bond order, the stronger the bond, and the shorter the bond length.

Problem 4 The data for N_2^+ in its $B^2\Sigma_u^+$ state (see Table VI) of the N_2^+ ion is intriguing. Why does this ion have the shortest bond length of any species in the table and also the highest vibrational frequency?

Looking at the NIST Chemistry Webbook, you can find additional excited states of N_2^+, namely the $a^4\Sigma_u^+$, $D^2\Pi_g$, and $C^2\Sigma_u^+$ states. What is a reasonable guess for the electronic configuration of each of these states?

Note that the 2nd column contains the nominal filling of the molecular orbitals, but not the actual Slater determinantal wavefunctions. Thus, the electronic configurations of all the listed O_2 states are identical, even though the three states correspond to the different electronic wavefunctions discussed in the section on the O_2 molecule.

IV. NEAR-HOMONUCLEAR DIATOMICS

When the two nuclei are no longer identical, there is no longer inversion symmetry, but the molecular orbitals still retain cylindrical symmetry. When the diatomic is nearly homonuclear, as, for example, in the CN, CO, or NO molecules the g/u symmetry is lifted. Usually, the lower energy molecular orbital being localized slightly more strongly on the atom with the higher atomic number. This is illustrated in Figs. 16 and 17, which compare for N_2 and CO the bonding 5σ ($3\sigma_g$ in the case of N_2) and bonding 1π ($1\pi_u$ in the case of N_2) orbitals. Since the orbitals are not strongly distorted, the bonding characteristics are little changed as is seen in Tab VII.

TABLE VI. States, dominant electronic configurations, and spectroscopic constants for several homonuclear diatomic molecules and ions.[a]

System	State	Configuration	bo[b]	T_e[c,d]	ω_e[d]	R_e[e]
C_2	$X^1\Sigma_g^+$	$\ldots 2\sigma_u^2 3\sigma_g^0 1\pi_u^4$	2[f]	0	1855	1.243
	$a^3\Pi_u$	$\ldots 2\sigma_u^2 3\sigma_g^1 1\pi_u^1$	2	716	1641	1.312
	$b^3\Sigma_g^-$	$\ldots 2\sigma_u^2 3\sigma_g^0 1\pi_u^2$	2	6434	1470	1.369
C_2^-	$X^2\Sigma_g^+$	$\ldots 2\sigma_u^2 3\sigma_g^1 1\pi_u^4$	2.5	0	1781	1.268
N_2^+	$X^2\Sigma_g^+$	$\ldots 2\sigma_u^2 3\sigma_g^1 1\pi_u^4$	2.5	0	2207	1.116
	$A^2\Pi_u$	$\ldots 2\sigma_u^2 3\sigma_g^2 1\pi_u^3$	2.5	9167	1904	1.175
	$B^2\Sigma_u^+$	$\ldots 2\sigma_u^1 3\sigma_g^2 1\pi_u^4$	3.5	25461	2420	1.074
N_2	$X^1\Sigma_g^+$	$\ldots 3\sigma_g^2 1\pi_u^4$	3	0	2359	1.098
	$A^3\Sigma_u^+$	$\ldots 3\sigma_g^1 1\pi_u^4 3\sigma_u$	2	50200	1460	1.287
N_2^-	$X^2\Pi_g$	$\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g$	2.5	0	1968	1.19
O_2^+	$X^2\Pi_g$	$\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g$	2.5	0	1905	1.116
O_2	$X^3\Sigma_g^-$	$\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g^2$	2	0	1580	1.208
	$a^1\Delta_g$	$\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g^2$	2	7918	1484	1.216
	$b^1\Sigma_g^+$	$\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g^2$	2	13195	1433	1.227
O_2^-	$X^2\Pi_g$	$\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g^3$	1.5	0	1091	1.35
F_2^+	$X^2\Pi_g$	$\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g^3$	1.5	0	1073	1.322
F_2	$X^1\Sigma_g^+$	$\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g^4$	1	0	917	1.412

[a] Data from http://webbook.nist.gov.
[b] Bond order, see Eq. (16).
[c] T_e is the energy of the minimum in the potential energy curve above the minimum in the potential energy curve of the ground electronic state. Thus T_e for the ground state is 0.
[d] Energy in wavenumbers.
[e] Distance in Å.
[f] Because of the important contribution of the $\ldots 2\sigma_u^0 3\sigma_g^2 1\pi_u^4$ electron occupancy, the effective bond order in the $X^1\Sigma_g^+$ state is greater than 2 (see subsection III B 5)

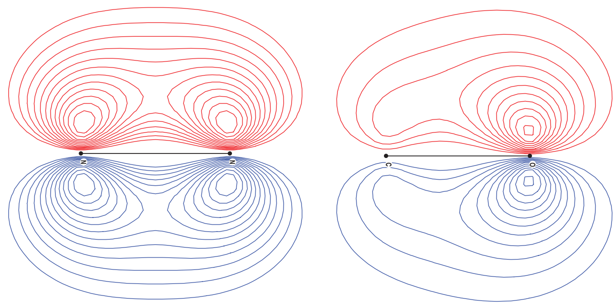

FIG. 16. Contour plots of the π bonding orbital in N_2 (left panel,$R = 2.09$) and CO (right panel, $R = 2.02$). In the latter case, the O atom is at the right.

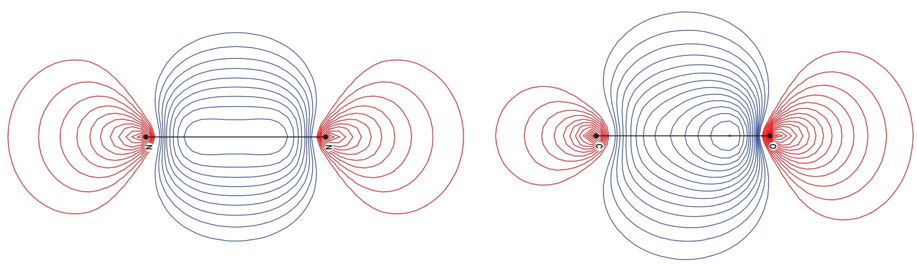

FIG. 17. Contour plots of the 5σ bonding orbital in N_2 (left panel, $R = 2.09$) and CO (right panel, $R = 2.02$). In the latter case, the O atom is at the right.

V. TRIATOMIC HYDRIDES

The simplest triatomic molecules are the HMH hydrides, where M designates any first-row atom. The most important is the HOH (water) molecule. The geometries of these molecules are specified by the two bond lengths and the bond angle, with the convention that a bond angle of 180^o corresponds to a linear arrangement of the atoms. The LCAO molecular orbitals are linear combinations of the two $1s$ orbitals on the hydrogens and one, or more, of the orbitals on the central atom. The electronic Hamiltonian is the standard sum of one-electron terms plus the two-electron repulsions. The one-electron term now contain the attraction between the electron and three nuclei, namely

$$h = \frac{1}{2}\nabla^2 - \frac{1}{r_{H1}} - \frac{1}{r_{H2}} - \frac{Z_M}{r_M}$$

The Hamiltonian is symmetric with respect to any rotation or reflection which leaves the geometry of the triatomic unchanged. Thus the molecular orbitals can be either symmetric or antisymmetric with respect to each of these operations. For a triatomic with equal bond

TABLE VII. States, dominant electronic configurations, and spectroscopic constants for several homonuclear and isoelectronic near-homonuclear diatomic molecules and ions.[a]

System	State	Configuration	bo[b]	T_e	ω_e[b]	R_e[c]
N_2^+	$X^2\Sigma_g^+$	$\ldots 2\sigma_u^2 3\sigma_g^1 1\pi_u^4$	2.5	0	2207	1.116
	$A^2\Pi_u$	$\ldots 2\sigma_u^2 3\sigma_g^2 1\pi_u^3$	2.5	9167	1904	1.175
	$B^2\Sigma_u^+$	$\ldots 2\sigma_u^1 3\sigma_g^2 1\pi_u^4$	3.5	25461	2420	1.074
CN	$X^2\Sigma^+$	$\ldots 4\sigma^2 5\sigma^1 1\pi^4$	2.5	0	2069	1.172
	$A^2\Pi$	$\ldots 4\sigma^2 5\sigma^2 1\pi^3$	2.5	9245	1813	1.233
	$B^2\Sigma^+$	$\ldots 4\sigma^1 5\sigma^2 1\pi^4$	3.5	25752	2164	1.15
N_2	$X^1\Sigma_g^+$	$\ldots 3\sigma_g^2 1\pi_u^4$	3	0	2359	1.098
	$A^3\Sigma_u^+$[d]	$\ldots 3\sigma_g^1 1\pi_u^4 3\sigma_u$	2	50200	1460	1.287
CO	$X^1\Sigma^+$	$\ldots 5\sigma^2 1\pi^4$	3	0	2169	1.128
	$a'^3\Sigma^+$	$\ldots 5\sigma^1 1\pi^4 6\sigma$	2	55825	1229	1.352
O_2^+	$X^2\Pi_g$	$\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g$	2.5	0	1905	1.116
NO	$X^2\Pi$	$\ldots 5\sigma^2 1\pi^4 2\pi_g$	2.5	0	1904	1.151
O_2	$X^3\Sigma_g^-$	$\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g^2$	2	0	1580	1.208
	$a^1\Delta_g$	$\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g^2$	2	7918	1484	1.216
	$b^1\Sigma_g^+$	$\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g^2$	2	13195	1433	1.227
NF	$X^3\Sigma^-$	$\ldots 5\sigma^2 1\pi^4 2\pi^2$	2	0	1141	1.317
	$a^1\Delta$	$\ldots 5\sigma^2 1\pi^4 2\pi^2$	2	12003	$\cdots$	1.308
	$b^1\Sigma+$	$\ldots 5\sigma^2 1\pi^4 2\pi^2$	2	18877	1197	1.227

[a] Data from http://webbook.nist.gov.
[b] Energy in wavenumbers; triple dots indicate the absence of an experimental value.
[c] Distance in Å; triple dots indicate the absence of an experimental value.
[d] Normally, excited states with a different multiplicity than that of the ground state are designated by lower-case letters. In the case of N_2, the excited states of singlet multiplicity (the multiplicity of the ground state) are designated by lower-case letters while the excited states of triplet (or higher) multiplicity are designated by upper-case letters.

lengths, and under the assumption that the molecule lies in the yz-plane, as shown in Fig. ?? these symmetry elements are a two-fold rotation around the z axis, designated C_2, a reflection in the xz-plane (the plane that bisects the molecule), designated σ_v, and a reflection in the yz-plane, dsignated σ'_v. The group of symmetry elements of a triatomic HMH hydride is designated C_{2v}. The symmetries of the possible molecule orbitals with respect to these three elements are labelled as shown in Table VIII. This table, which is called a "character table" equilibrium distances and dissociation energies. Here E designates the unit operator.

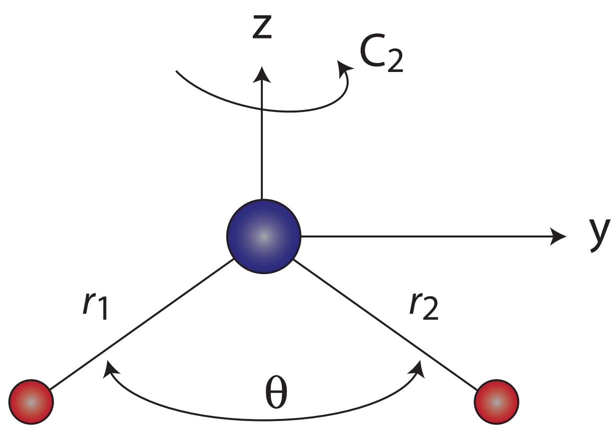

FIG. 18. Geometry of an HMH hydride. The symmetry elements are C_2, a two-fold rotation around the z axis; σ_v, a reflection in the xz-plane (the plane that bisects the molecule; and σ'_v, a reflection in the yz-plane (the plane containing the molecule).

TABLE VIII. Character table for C_{2v} symmetry.

Character	E	C_2	σ_v	σ'_v	linear, rotation	quadratic
a_1	+1	+1	+1	+1	z	x^2, y^2, z^2
a_2	+1	+1	−1	−1	R_z	xy
b_1	+1	−1	+1	−1	x, R_y	xz
b_2	+1	−1	−1	+1	y, R_x	yz

Thus any s orbital, any p_z, or the $d_{x^2-y^2}$ and d_{z^2} atomic orbitals on the C atom belong to the symmetry group a_1, the p_x and the d_{xz} orbitals belong to the symmetry group b_1, and the p_y and d_{yz} orbitals belong to the symmetry group b_2. Finally, the d_{xy} orbital belongs to the symmetry group a_2.

A further introduction to molecular symmetries and group theory is contained in the Molecular_symmetry Chapter in Wikipedia.

We can express, generally, the molecular orbitals of H_2O as linear combinations of the two H $1s$ orbitals as well as the atomic orbitals on the O. Note that since the molecular orbital must be symmetric or antisymmetric with respect to the C_2 and σ_v operations, we must take include both $1s_H$ orbitals with an equal, or opposite sign. This correspond to a_1 and b_2 symmetry, namely

$$1s_H(a_1) = [1s_1 + 1s_2] \tag{24}$$

and

$$1s_H(b_2) = [1s_1 - 1s_2] \tag{25}$$

Thus, we have 7 atomic orbitals (a_1 symmetry: $1s, 2s, 2p_z, 1s_{\mathrm{H}}(a_1)$), b_2 symmetry: $2p_y, 1s_{\mathrm{H}}(b_2)$, and b_1 symmetry $2p_x$). Note that there are no atomic orbitals of a_2 symmetry, since there are no d orbitals in the valence basis. Within the Hartee-Fock approximation, the ground electronic state of the H_2O molecule is approximated by placing the 10 electrons 2×2 into the five lowest energy molecular orbitals. These are, to first order, the $1s$ and $2s$ orbitals on the O atom, as well as the bonding combination of $1s_{\mathrm{H}}(a_1)$ and $2p_z$, followed by the bonding combination of the $1s_{\mathrm{H}}(b_2)$ and $2p_x$. The remaining two electrons go into the $2p_y$ orbital on the O, which is pointed out of the plane. This orbital is antisymmetric with respect to reflection in the plane of the molecule (σ_v') and so will no mix with the linear combination of the $1s$(H) orbitals, both of which are symmetric with respect to σ_v'.

Consequently, the electron occupancy of H_2O is

$$\psi = \left|1a_1^2 2a_1^2 3a_1^2 1b_2^2 1b_1^2\right| \approx \left|1s_{\mathrm{O}}^2 2s_{\mathrm{O}}^2 3a_1^2 1b_2^2 2p_y^2\right|$$

Since all the orbitals are doubly filled, the overall wavefunction of the ground state of H_2O is fully symmetric, with spin zero. The lowest electronic state of H_2O is designated ${}^1\tilde{A}_1$. Here, the tilde indicates that we are referring to a triatomic molecule. With this electron occupancy, one determines the best one-electron functions, by allowing each electron to move in the average field of all the nine others. Figure 19 shows the dependence on the bond-angle of (left panel) the total electronic energy of H_2O and (right panel) the orbital energies. The orbitals themselves are shown in Figs. 20, 21, 22, and 23. Note that the orbitals shown in Figs. 20, 21, 22 lie in the plane of the H_2O molecule while the orbital shown in Fig. 23 is *perpendicular* to this plane.

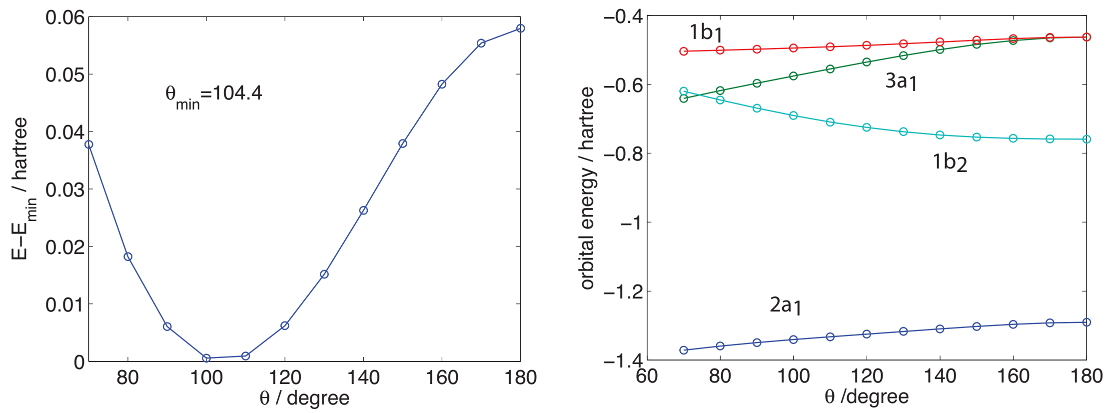

FIG. 19. (left panel) Energy of the H_2O molecule in the $1\tilde{A}_1$ state as a function of the bond angle, from Hartree-Fock calculations with a double-zeta basis set. The energy at the minimum is –76.03 hartree. (right panel) Energies (in hartree) of the orbitals of the H_2O molecule (with the exception of the $1s_{\rm O}$ orbital) as a function of the bond angle.

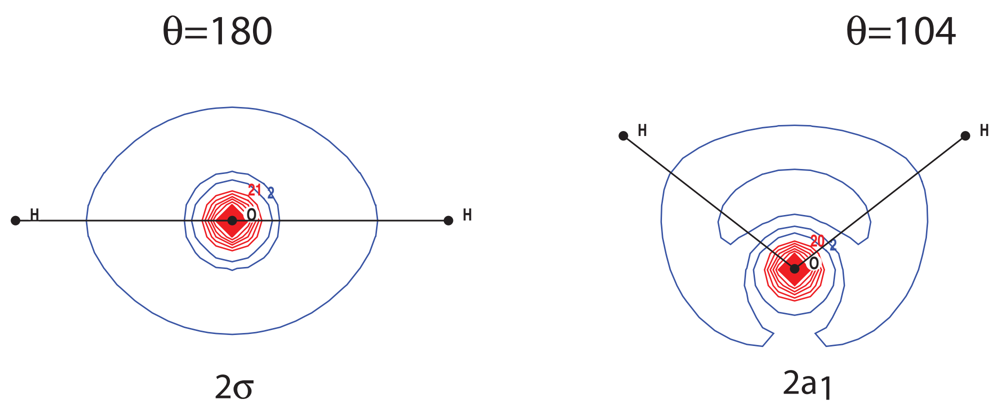

FIG. 20. Contour plot of the 2σ ($2a_1$) orbital of H_2O in linear (left panel) and bent (right panel) geometry.

We observe that the 2σ orbital is barely delocalized, very similar to the $2s$ orbital on the O atom. The 3σ orbital, which is a linear combination of the $2p_y$ orbital on the O (see Fig. 18) and the antisymmetric linear combination of the two H $1s$ orbitals [Eq. (25)] is bonding in both bent and linear geometries. By contrast, the 1π orbital, which is of π symmetry in colinear geometry, does not contribute to bonding in linear geometry. It is a "non-bonding" orbital. However, when the molecule bends (right panel of Fig. 22) the $2p_z$ O orbital can mix constructively with the symmetric linear combination of the two H $1s$ orbitals [Eq. 24)] and thus contribute to bonding. For this reason the energy of this orbital decreases dramatically as the molecule bends (this can be seen in the right panel of Fig. 19.

There is one more doubly-filled orbital in H_2O. This orbital corresponds to the out of plane $2p_x$ orbital on the O atom. It has symmetry π_x in linear geometry and b_1 in bent geometry. This orbital never contributes to bonding. The two electrons in this orbital are called, hence, a "lone-pair". The geometry of the H_2O molecule can not be predicted on

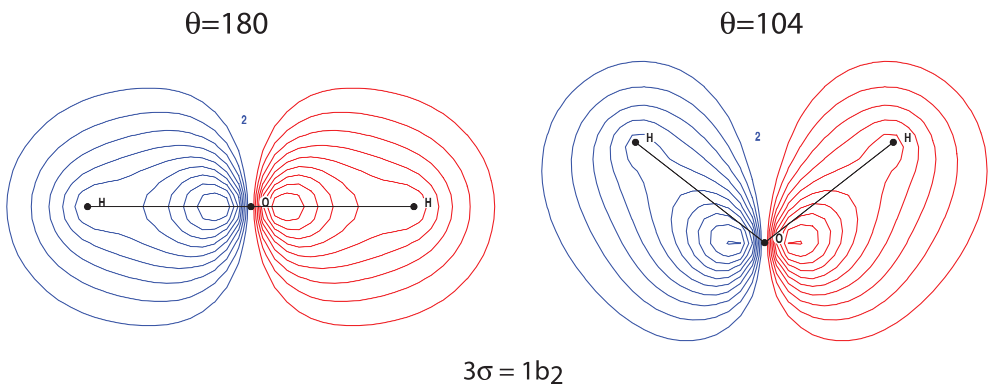

FIG. 21. Contour plot of the $3\sigma\,(1b_2)$ orbital of H_2O in linear (left panel) and bent (right panel) geometry.

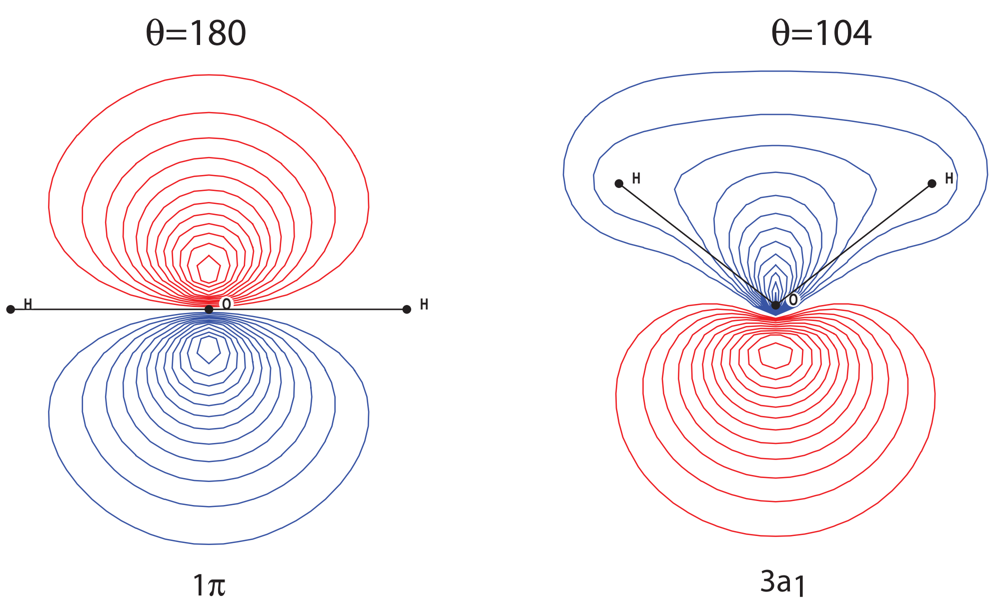

FIG. 22. Contour plot of the $3\sigma\,(3a_1)$ orbital of H_2O in linear (left panel) and bent (right panel) geometry.

the basis of simple Lewis dot structures. Further, in the usual partial-charge model of water (see Fig. 24) the positive charges on the protons should repel one-another which would lead

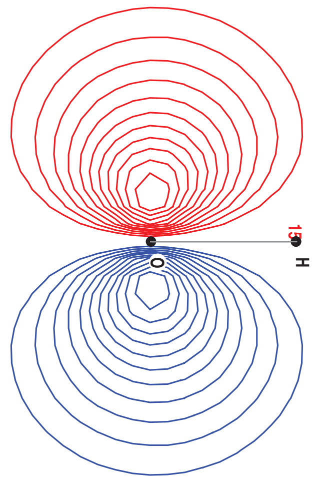

FIG. 23. Contour plot of the $1\pi, (1b_1)$ orbital of H_2O in bent geometry. This non-bonding orbital is perpendicular to the plane of the molecule, which is shown here edge on. This orbital changes very little as the H_2O molecule bends.

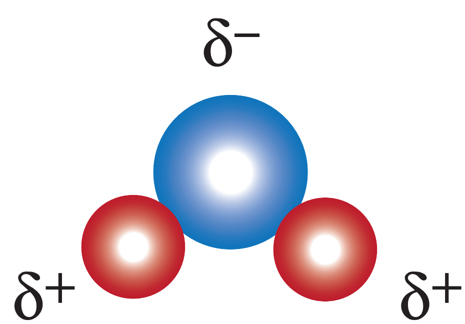

FIG. 24. Partial-charge model of H_2O

to a prediction of linear structure. In fact, however, because the two electrons in the 3σ orbital are non-bonding when the molecule is linear but bonding when the molecule is bent, H_2O prefers a bent geometry.

This is an illustration of what are called Walsh's rules. These qualitative "rules" predict that the linear or bent structure of triatomic HMH hydrides depends on the occupancy of the $1\pi\,(1b_2)$ orbital, which becomes a bonding orbital only when the molecule is bent. However, chemistry is very subtle, and Walsh's rules are simplistic. We see in the right panel of Fig. 19 that although the energy of the $3\sigma\,(3a_1)$ orbital decreases as the molecule bends, the energy of some of the other orbitals increase, in particular the σ orbital (Fig. 21) which is a combination of the $2p_y$ orbital on the central atom and the antisymmetric combination

[Eq. 25)] of the two H $1s$ orbitals. However, as shown if Fig. 25 In fact, when we sum the energies of these two orbitals ($3a_1$ and $1b_2$) and multiply by two (the occupancy of each orbital), the bent geometry is favored.

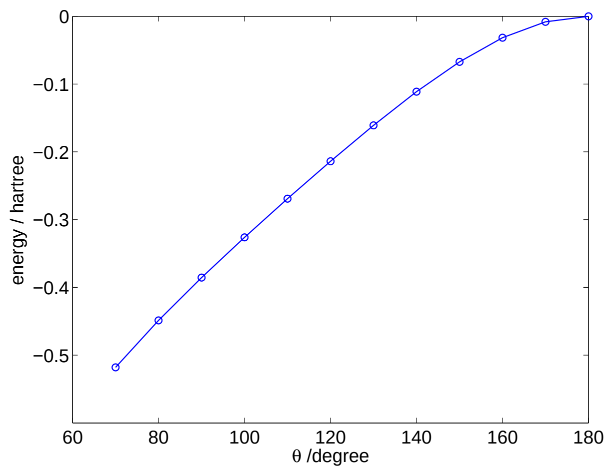

FIG. 25. The sum of the orbital energies of the $3a_1$ and $1b_2$ orbitals of H_2O (see the right panel of Fig. 19), multiplied by two, as a function of the HOH angle.

Problem 5 Consider the CH_2 molecule, called the methylene radical. Assume the $1s\,(1a_1)$ and $2s\,(2a_1)$ orbitals are doubly filled. Using a tableau method write down all the possible states with bond order 2 that you can get by distributing the 4 valence electrons among the $3a_1$, $1b_1$, and $1b_2$ orbitals. Give Slater determinantal wavefunctions for each of these states. Label each state as ${}^{2S+1}X$ where X is the overall symmetry character of the state ($X = A_1$, A_2, B_1, B_2). This overall symmetry character can be obtained by multiplying together the symmetries of any singly-filled orbitals and then consulting Tab VIII (Any doubly filled orbitals are always fully symmetric).

Then, predict the geometry of all the states and predict which state will lie lowest in energy.

The first electronically excited state of water corresponds to excitation of an electron out of the highest filled bonding orbital (the $1b_1$ orbital, see the right panel of Fig. 19, to the lowest unfilled orbital, which is an orbital of a_1 symmetry shown in Fig. 26. This orbital is antibonding, because it has a node between the H and the O atoms. This excited state then has the electron occupancy $\psi = |1a_1^2 2a_1^2 3a_1^2 1b_2^2 1b_1 4a_1|$ and is therefore either a singlet

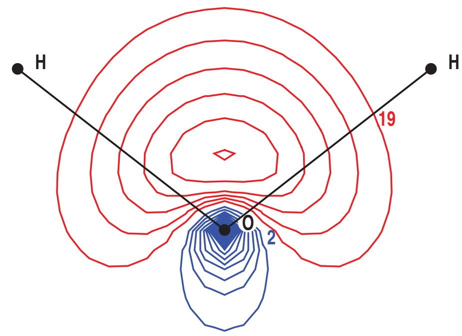

FIG. 26. Contour plot of the 4σ $(3a_1)$ orbital of H_2O in bent geometry.

or triplet state with overall B_1 symmetry, since the product of the character table entries for a singly filled b_1 and a singly-filled, totally symmetric a_1 orbital has b_1 symmetry.

In fact, because we have excited an electron into an orbital of antibonding character, the energy decreases as one of the OH bonds is allowed to lengthen, which destroys the C_{2v} symmetry. Eventually, the energy keeps decreasing until one of the OH bonds is broken. Thus the B_1 state of water is repulsive, and excitation of this state leads to dissociation of the molecule.

VI. ROVIBRONIC STATES OF DIATOMIC MOLECULES

A. Wavefunctions

The atoms in a diatomic molecule will be bound if the potential curve of the diatomic possesses a minimum at a finite value of R. The position of the nuclei in space is a 6-dimensional vector $(x_a, y_a, z_a, x_b, y_b, z_b)$. As discussed in more detail in Appendix F, these can be reexpressed in terms of the positions of the center of mass $\vec{\mathcal{R}} = \vec{\mathcal{X}}, \vec{\mathcal{Y}}$, and $\vec{\mathcal{Z}}$, where

$$\vec{\mathcal{X}} = \frac{m_a\vec{X}_a + m_b\vec{X}_b}{m_a + m_b} = \frac{m_a\vec{X}_a + m_b\vec{X}_b}{M}$$

and, likewise, for $\vec{\mathcal{Y}}$ and $\vec{\mathcal{Z}}$, and the relative position of the two nuclei $[\vec{R} = \vec{X}, \vec{Y}, \vec{Z}]$, where $\vec{X} = \vec{X}_b - \vec{X}_a$ and likewise for $\vec{Y}$ and $\vec{Z}$. Note that here we use script uppercase to denote the position of the center of mass and plain upper case to denote the relative position of the two nuclei. In Appendix F the center-of-mass and relative coordinates are denoted by upper case and lower case. As discussed in Sec. I A, and in the absence of an external field, the potential depends only on the magnitude of $\vec{R}$. The Hamiltonian is separable so that the wavefunction for the motion of the two nuclei can be written as a product of the wavefunction for the position of the center-or-mass $\Psi(\mathcal{X}, \mathcal{Y}, \mathcal{Z})$ multiplied by the wavefunction for the relative motion of the two nuclei $\psi(X, Y, Z)$. The energy is the sum of the energy associated with the motion of the center of mass and the energy associated with the relative motion, namely

$$-\frac{1}{2M}\nabla^2_{\mathcal{R}}\Psi(\mathcal{X}, \mathcal{Y}, \mathcal{Z}) = E_{CM}\Psi(\mathcal{X}, \mathcal{Y}, \mathcal{Z}) \tag{26}$$

and

$$\left[-\frac{1}{2\mu}\nabla^2_R + V^{(k)}_{eff}(R)\right]\psi(X, Y, Z) = E_{int}\psi(X, Y, Z) \tag{27}$$

Here $V^{(k)}_{eff}(R)$ is the effective (Born-Oppenheimer) potential in the k^{th} electronic state for the motion of the nuclei: the sum of the electronic energy plus the repulsion between the two nuclei.

The motion of the center of mass is that of a particle in a cubic box (no potential), so that the motion of the molecule in space has the same wavefunctions and energies as that of a particle in a box with mass equal to the total mass of the molecule. We shall label the wavefunction by the three particle-in-a-box quantum numbers, namely $\Psi_{N_{\mathcal{X}}, N_{\mathcal{Y}}, N_{\mathcal{Z}}}$.

In Eq. (27), the potential depends only on the distance between the two nuclei. Thus, as in the case of the hydrogen atom, the Hamiltonian is separable in spherical polar coordinates. The wavefunction may be written as the product of a spherical harmonic in the angular degrees of freedom (the orientation of $\vec{R}$) multiplied by a function which depends only on R (you may be more familiar with this as the radial function $\mathcal{R}(R)$ in the case of the hydrogen atom) which satisfies the equation

$$\left[-\frac{1}{2\mu R^2}\frac{d}{dR}\left(R^2\frac{d}{dR}\right) + \frac{j(j+1)}{2\mu R^2} + V^{(k)}_{eff}(R)\right]\chi_{vj}(R) = E_{int}\chi_{vj}(R) \tag{28}$$

The complete wavefunction is then

$$\Xi(\mathcal{X}, \mathcal{Y}, \mathcal{Z}, R, \Theta, \Phi, \vec{r}) = \Psi_{N_{\mathcal{X}}, N_{\mathcal{Y}}, N_{\mathcal{Z}}}(\mathcal{X}, \mathcal{Y}, \mathcal{Z})\psi_{k,v,j,m}(X, Y, Z)$$

where

$$\psi_{k,v,j,m}(X, Y, Z) = Y_{jm}(\Theta, \Phi)\chi_{vj}(R)\chi^{(k)}_{el}(\vec{r}; R) \tag{29}$$

where $\vec{r}$ denotes collectively the coordinates of all the electrons. Here k is the electronic state index (or quantum number), v is the vibrational quantum number, j is the rotational quantum number, and m is the projection of the rotational angular momentum ($-m \leq j\ m$).

If the potential curve $V_{eff}^{(k(}(R)$ has a minimum, then the internal energy (the molecular energy independent of the motion of its center of mass through space) will correspond to a particular electronic-vibration-rotation (or "rovibronic") state, which we label with the quantum numbers $\{k, v, j, m\}$, where m is the projection of $\vec{j}$.

B. Energies

To determine these internal energies of the diatomic molecule, we need to solve Eq. (27). An analytic solution is not possible for most realistic molecular potentials. To approximate the energies, we expand the potential about $R = R_e$, the minimum in $V_{eff}^{(k)}$, namely

$$V(R) \approx V(R_e) + \frac{1}{2}\left.\frac{d^2V}{dR^2}\right|_{R_e} x^2 + \frac{1}{6}\left.\frac{d^3V}{dR^3}\right|_{R_e} x^3 + \frac{1}{24}\left.\frac{d^4V}{dR^4}\right|_{R_e} x^4 + \ldots$$

where $x \equiv R - R_e$ and where, for simplicity, we have suppressed the subscript "eff" and superscript (k). Note that the first derivative of the potential vanishes at $R = R_e$. We can also expand the rotational angular momentum term depending on $1/R^2$ by noting that

$$\frac{1}{R^2} = \frac{1}{(R_e + x)^2} = \frac{1}{R_e^2(1 + x/R_e)^2} \approx \frac{1}{R_e^2}\left(1 - \frac{x}{R_e} + 2\frac{x^2}{R_e^2} - 3\frac{x^3}{R_e^3} + 4\frac{x^4}{R_e^4} + \ldots\right)$$

We can now use time-independent perturbation theory, so that

$$E_{int} \approx E^{(0)} + \left\langle \phi_v^{(0)} \right| H' \left| \phi_v^{(0)} \right\rangle$$

We separate the Hamiltonian as

$$H_o = \frac{j(j+1)}{2\mu R_e^2} + V(R_e) + \frac{1}{2}\left.\frac{d^2V}{dR^2}\right|_{R_e} x^2$$

and

$$H' = \frac{j(j+1)}{2\mu R_e^2}\left(-\frac{x}{R_e} + \frac{x^2}{R_e^2} - \frac{x^2}{R_e^3} + \frac{x^4}{R_e^4}\right) + \frac{1}{6}\left.\frac{d^3V}{dR^3}\right|_{R_e} x^3 + \frac{1}{24}\left.\frac{d^4V}{dR^4}\right|_{R_e} x^4 \qquad (30)$$

Thus, the zero-order wavefunctions and energy levels are those of a Harmonic oscillator with force constant

$$k = \left.\frac{d^2V}{dR^2}\right|_{R_e}$$

and energies [note that the term $j(j+1)/(2\mu R_e^2)$ leads to a j-dependent addition to the energy]

$$E^{(0)}_{v,j} = V(R_e) + Bj(j+1) + \left(v + \frac{1}{2}\right)\hbar\omega \tag{31}$$

where the rotational constant B_e is defined by (here, for generality, we have included explicitly the factor of $\hbar$)

$$B = \frac{\hbar^2}{2\mu R_e^2}$$

and the vibrational frequency is defined by $\omega = \sqrt{k/\mu}$. Typically, the potential is defined so that

$$\lim_{R\to\infty} V(R) = 0$$

so that $V(R_e) = -\mathcal{D}_e$, where $\mathcal{D}_e$ is the dissociation energy of the molecule, which is defined as a positive number. Thus, we can rewrite Eq. (31) as

$$E^{(0)}_{v,j} = -\mathcal{D}_e + Bj(j+1) + \left(v + \frac{1}{2}\right)\hbar\omega \tag{32}$$

The first-order correction to the energy is

$$\begin{aligned} E^{(1)}_{v,j} = \langle v|\, H' \,|v\rangle = \langle v|\, \frac{j(j+1)}{2\mu R_e^2}\left[-\frac{x}{R_e} + 2\frac{x^2}{R_e^2} + 3\frac{x^3}{R_e^3} - 4\frac{x^4}{R_e^4}\right]|v\rangle \\ + \langle v|\, \frac{1}{6}\left.\frac{d^3V}{dR^3}\right|_{R_e} x^3 + \frac{1}{24}\left.\frac{d^4V}{dR^4}\right|_{R_e} x^4 + \ldots |v\rangle \end{aligned} \tag{33}$$

By symmetry $\langle v|x|v\rangle = \langle v|x^3|v\rangle = 0$. From the Matlab script quartic_oscillator_variational.m, you can show that

$$\langle v|x^2|v\rangle = (v+1/2)\frac{\hbar}{\sqrt{k\mu}} = (v+1/2)\frac{\hbar}{\mu\omega} \tag{34}$$

and

$$\langle v|x^4|v\rangle = \left[12(v+1/2)^2 + 3\right]\frac{\hbar^2}{8k\mu} = \left[12(v+1/2)^2 + 3\right]\frac{\hbar^2}{8(\mu\omega)^2}. \tag{35}$$

Thus,

$$E_{v,j}^{(1)} = \hbar \frac{(v+1/2)j(j+1)}{R_e^4 \mu^{3/2} k^{1/2}} + \hbar^2 \left[\frac{1}{24} \left. \frac{d^4V}{dR^4} \right|_{R_e} + \frac{j(j+1)}{2\mu R_e^6} \right] \left[\frac{12(v+1/2)^2 + 3}{8k\mu} \right] \tag{36}$$

Problem 6 Use the Matlab script quartic_oscillator_variational.m to generate expressions for $\langle v|x^4|v\rangle$ for $v = 0-5$. Show that they correspond to the analytic formula given in Eq. (35).

To evaluate the second-order contributions to the energy, we need the off-diagonal matrix elements of x^n ($n = 1-4$) in the harmonic oscillator basis. In general a term in x^n in H' [Eq. 30)] will make a second-order contribution of

$$E_{vj}^{(2)} = \sum_{v' \neq v} \frac{|\langle v|x^n|v'\rangle|^2}{E_v - E_{v'}} = \sum_{v' \neq v} \frac{|\langle v|x^n|v'\rangle|^2}{(v-v')\omega}$$

The Hermite polynomials satisfy a two-term recursion relation

$$xH_m(x) = \frac{1}{2}H_{m+1}(x) + mH_{m-1}(x)$$

Thus, acting on $H_m(x)$ by x^n will generate polynomials up to order $H_{m+n}(x)$. Consequently, the orthogonality and symmetry properties of the Hermite polynomials will guarantee that

$$\langle v| x^n |v'\rangle = 0 \,\mathrm{for}\, v' > v + n$$

Furthermore, by symmetry, if n is odd then

$$\langle v| x^n |v'\rangle = 0$$

if v and v' are both odd or both even. Similarly, if n is even, then the matrix element will vanish if v is odd and v' is even, or vice versa. The script quartic_oscillator_variational.m generates the matrices $\langle v|x^n|v'\rangle$ for $0 \leq v \leq 6$ and $n = 1-4$. From the output of this script, specifically the matrix `x1mat`, you can show that, for $v' > v$

$$\begin{aligned} \langle v|x|v'\rangle &= \left[\frac{2(v+1/2)+1}{4k\mu} \right]^{1/2}, \,\mathrm{for}\, v' = v+1 \\ &= 0, \text{ otherwise} \end{aligned} \tag{37}$$

(with a similar relation when $v' < v$). Likewise, from the matrix `x2mat` you can show that, for $v' > v$

$$\begin{aligned}\langle v|x^2|v'\rangle &= \left[\frac{4(v+1/2)^2 + 8(v+1/2) + 3}{16k\mu}\right]^{1/2}, \text{ for } v' = v+2 \\ &= 0, \text{ otherwise}\end{aligned} \tag{38}$$

Similarly, from the matrix `x3mat` you can show that, for $v' > v$

$$\begin{aligned}\langle v|x^3|v'\rangle &= \left[\frac{72(v+1/2)^3 + 108(v+1/2)^2 + 54(v+1/2) + 9}{64k\mu}\right]^{1/2}, \text{ for } v' = v+1 \\ &= \left[\frac{8(v+1/2)^3 + 36(v+1/2)^2 + 46(v+1/2) + 15}{64k\mu}\right]^{1/2}, \text{ for } v' = v+3 \\ &= 0, \text{ otherwise}\end{aligned} \tag{39}$$

Examining the equations for the zeroth and first-order energies, we see that the total internal energy of a diatomic can be expressed, most generally then as a dual power series in $(v+1/2)$ and $j(j+1)$, namely

$$\begin{aligned}E_{v,j} = &-\mathcal{D}_e + Y_{00} + Y_{10}(v+1/2) + Y_{01}j(j+1) + Y_{11}(v+1/2)j(j+1) \\ &+Y_{20}(v+1/2)^2 + Y_{21}j(j+1)(v+1/2)^2 + \ldots\end{aligned} \tag{40}$$

The Y_{mn} coefficients are called Dunham Coefficients. In principle, by means of perturbation theory one can relate the values of these coefficients to the physical parameters which define the molecular potential $V(R)$ as well as the reduced mass of the molecule. Alternatively, spectroscopists often fit the results of experiments to the following (virtually identical) double power series

$$\begin{aligned}E_{v,j} = &(v+1/2)\omega_e - (v+1/2)^2\omega_e x_e + (v+1/2)^3\omega_e y_e \\ &+j(j+1)B_e - j(j+1)(v+1/2)\alpha_e\end{aligned} \tag{41}$$

Note that the coefficient α_e is unrelated to the parameter α which appears in the expression for the harmonic oscillator wavefunctions. We can combine the last two terms in Eq. (41 to obtain

$$E_{v,j} = \ldots + j(j+1)B_e - j(j+1)(v+1/2)\alpha_e = \ldots + j(j+1)B_v$$

where B_v, the effective rotational constant in vibrational level v is

$$B_v = B_e - \alpha_e(v + 1/2)$$

The expansion coefficients in Eq. (41), often called "spectroscopic coefficients", as well as the Dunham coefficients, are typically given in cm^{-1} units, so that the resulting "energy" is proportional to the level energy but needs to be multiplied by hc to obtain the a result in units of energy.

C. Physical interpretation of the spectroscopic expansion coefficients

The Dunham coefficients can be related by perturbation theory to the reduced mass of the molecule and to the derivatives of the potential curve, while the expansion coefficients of Eq. (41) are empirical parameters. However, the two expansions are closely related. In particular:
i. Y_{10} (or ω_e) is the vibrational frequency of the molecule, related to the curvature (the second derivative) of the potential $V_{eff}(R)$ at its minimum. Since, for a classical oscillator, $\omega = \sqrt{k/\mu}$, for chemically indentical, but isotopically distinct, species (such as HF/DF or $^{12}CO/^{13}CO$) the vibrational frequency is proportional to the inverse square root of the reduced mass. For diatomic hydrides ω_e is typically between 3000 and 4000 cm^{-1}. For non-hydride diatomics ω_e is typically between 1000 and 2500 cm^{-1}.
ii. Y_{20} (or $\omega_e x_e$) is the effect of the anharmonicity of $V_{eff}(R)$, resulting in a decrease in the vibrational energy spacing as the vibrational quantum number increases. Note that the $\omega_e x_e$ term in Eq. (41) occurs with a negative sign, whereas in the Dunham expansion [Eq. (40)] the Y_{20} term enters with a positive sign. In nearly all cases $\omega_e x_e$ is positive and, correspondingly, Y_{20} is negative. Typically, $\omega_e x_e$ is $1/20 - 1/10$ of the value of the vibrational frequency.
iii. Y_{30} (or $\omega_e y_e$) is a higher-order harmonic correction. The value of $\omega_e y_e$ is always very small.
iv. Y_{01} (or B_e) is the rotational constant, related, inversely, to the square of the bond length at equilibrium. For chemically indentical, but isotopically distinct, species the vibration frequency is proportional to the inverse of the reduced mass. Typically, for hydrides, B_e

is on the order of tens of wavenumbers. For non-hydride diatomics, B_e is typically on the order of 1–2 cm^{-1}.

Extraction of B_e from an experiment is the best way to determine the bond length of a molecule. For polyatomic molecules, most rotational transitions lie in the microwave region of the spectrum. Advances in microwave technology, stimulated by the large investment in radar during the 2nd World War, allowed the determination of the geometry (bond lengths and bond angles) of many small polyatomic molecules. By isotopic substitution of the parent molecule, which generated a different pattern of rotational levels, and, hence, different rotational constants, one could determine geometries of even complex molecules without ambiguity.

v. Y_{11} (or α_e) is the change in the rotational constant upon vibrational excitation. A rotating, vibrating molecule has an effective rotational constant $B_v = \langle v|1/(2\mu R^2)|v\rangle$. As the vibrational quantum number increases, because of the anharmonicity of the molecular potential the wavefunction will extend to larger and larger values of R. Thus, the effective value of $1/R^2$ (and, hence, the rotational constant) will become smaller. Note that the α_e term in Eq. (41) occurs with a negative sign, whereas in the Dunham expansion [Eq. (40)] the Y_{11} term enters with a positive sign. In nearly all cases α_e is positive and, correspondingly, Y_{11} is neagtive. For most molecules, the magnitude of α_e is 1–2% the value of the rotational constant.

vi. A smaller term which we have not included in Eqs. (40) and (41) is called the centrifugal distortion constant [Y_{02} or D_e (no relation to the dissociation energy)]. As the molecule rotates faster and faster, the increasing size of the $j(j+1)/2\mu R^2$ term in Eq. (28) will shift the minimum in the potential to larger values of R. This will result in a slight decrease in the effective rotational constant. The constants Y_{02} and D_e are, consequently, negative. Typically the magnitude of D_e is no larger than 1% of the magnitude of B_e.

vi. The constant term Y_{00} does not appear in the most common spectroscopic expansion [Eq. (41)]. Since the Y_{00} term affects equally the energy of any vibration-rotation level, it is difficult to deduce from a spectroscopic experiment which measures differences between energy levels. Both Y_{00} and the dissociation energy $\mathcal{D}_e$ provide the constant term in the expansion of Eq. (40). However, the magnitude of Y_{00} is a very small fraction of molecular dissociation energies which are typically 50,000 – 100,000 cm^{-1}. Usually, molecular dissociation energies are deduced by thermochemical measurements (heats of reaction, heats of formation). Consequently, one would need extremely high precision in these thermochemical measurements to allow an accurate determination of Y_{00}.

Problem 7 For the H_2 molecule, $R_e = 0.74144\,\mathring{A}$, $\omega_e = 4401.2\,\mathrm{cm}^{-1}$, and $\mathcal{D}_e = 38297\,\mathrm{cm}^{-1}$. Determine the parameter β (in bohr^{-1}) in a Morse fit to the potential curve for H_2

$$V(R) = \mathcal{D}_e \left\{\exp\left[-2\beta(R-R_e)\right] - 2\exp\left[-\beta(R-R_e)\right]\right\}$$