

Quantum Chemistry 2 Notes

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1 Preliminaries

Once there are molecules, chemistry begins. This is going to be quantum mechanics of molecules.

1.1 Approximation Methods

We begin with a discussion of approximation methods. Note that we cannot use perturbation theory to get good quantitative results, so we need to use other methods, one of which is the variation method which says that

$$E_{var} = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\int d\tau \phi^* H(r) \phi(r)}{\int d\tau \phi^*(r) \phi(r)} > E_0. \quad (1.1)$$

This relies on a good trial wavefunction, but sets an upper bound on the energy. Generally, we use linear expansion terms for the wavefunction. Say you guess a trial wavefunction

$$\phi(x) = ae^{-x^2} + bxe^{-x^2} + cx^2e^{-x^2}, \quad (1.2)$$

and what we want is

$$\frac{\partial E_{var}}{\partial a} = \frac{\partial E_{var}}{\partial b} = \frac{\partial E_{var}}{\partial c} = 0. \quad (1.3)$$

This can also be used to calculate excited states.

1.2 Electronic Structure of Atoms

We will start with Hydrogen and then move on to Helium. At some point we will get to Carbon. States of Carbon are important for qualification.

1.3 Molecules

We are going to build up the molecular wavefunction and then talk about spectroscopy of molecules.

1.4 Atomic Units

One annoying thing about quantum mechanics is that there is \hbar everywhere and this makes the scale of numbers interesting. So we are going to set $\hbar = 1$ and $m_e = 1$ and work in this picture. This system is called atomic units. All that is important to know at this point is the conversion factor to normal units. In most experimental determinations of quantum mechanics, we are looking at an energy difference ΔE . What is measured experimentally is a wavelength or a frequency,

$$\Delta E = h\nu = \hbar\omega = \frac{hc}{\lambda} \quad (1.4)$$

This gives rise to the use of frequency units or wavenumbers. Which unit is used is dependant on the area of the spectrum under study.

2 Approximation Methods

2.1 Perturbation Theory

Perturbation theory is based on the idea that if I have some Hamiltonian operator \hat{H} , I can separate it in to

$$\hat{H}_0 + \underbrace{\lambda H'}_{\text{perturbation}}, \quad (2.1)$$

where λ is between 0 and 1 and controls the strength of the perturbation. So if we look at a quartic oscillator which has a potential

$$V(x) = \frac{1}{2}k_4x^4, \quad (2.2)$$

and we want to solve the Hamiltonian

$$\hat{H} = -\frac{1}{2m} \frac{d^2}{dx^2} + V(x). \quad (2.3)$$

Then we can use the harmonic oscillator as our unperturbed Hamiltonian. So we get that

$$\hat{H}_0 = -\frac{1}{2m} \frac{d^2}{dx^2} + \frac{1}{2}kx^2 \quad (2.4)$$

$$H' = \frac{1}{2}(k_4x^4 - kx^2). \quad (2.5)$$

Now we can solve the Shrodinger equation

$$\hat{H}_0\phi_n^{(0)} = E_n^{(0)}\phi_n^{(0)}, \quad (2.6)$$

with the known harmonic oscillator solution to get the lowest order wavefunctions. So we can then expand the wavefunction as a power series in λ to get

$$\psi_n = \phi_n^{(0)} + \lambda\phi_n^{(1)} + \lambda^2\phi_n^{(2)} + \dots \quad (2.7)$$

So we can solve the Shrodinger equation

$$\hat{H}\psi_n = E_n\psi_n, \quad (2.8)$$

and the energy is given as

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad (2.9)$$

We will plug our expansion for ψ into the Shrodinger equation and then group terms. We can solve by knowing that the terms with equal powers of λ . So we get

$$(\hat{H}_0 + \lambda H')(\phi_n^{(0)} + \lambda\phi_n^{(1)} + \lambda^2\phi_n^{(2)} + \dots) = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots)(\phi_n^{(0)} + \lambda\phi_n^{(1)} + \lambda^2\phi_n^{(2)} + \dots), \quad (2.10)$$

which gives rise to the equations

$$\begin{aligned} \hat{H}_0\phi_n^{(0)} &= E_n^{(0)}\phi_n^{(0)} \\ H'\phi_n^{(0)} + \hat{H}_0\phi_n^{(1)} &= E_n^{(1)}\phi_n^{(0)} + E_n^{(0)}\phi_n^{(1)} \\ &\vdots \end{aligned} \quad (2.11)$$

So now we can expand the function in a complete set of states which we already know as

$$\phi_n^{(1)} = \sum_{k \neq n}^{\infty} c_{nk} \phi_k^{(0)}, \quad (2.12)$$

which gives rise to

$$H' \phi_n^{(0)} + \hat{H}_0 \sum_{k \neq n}^{\infty} c_{nk} \phi_k^{(0)} = E_n^{(1)} \phi_n^{(0)} + E_n^{(0)} \sum_{k \neq n}^{\infty} c_{nk} \phi_k^{(0)}. \quad (2.13)$$

Since any operator commutes with a constant, we get that

$$H' \phi_n^{(0)} + \sum_{k \neq n}^{\infty} c_{nk} E_k^{(0)} \phi_k^{(0)} = E_n^{(1)} \phi_n^{(0)} + \sum_{k \neq n}^{\infty} c_{nk} E_k^{(0)} \phi_k^{(0)}. \quad (2.14)$$

Now using the fact that $\{\phi_n^{(0)}\}$ are normalized and orthogonal and multiplying by $(\phi_n^{(0)})^*$ we get that

$$\langle \phi_n^{(0)} | H' | \phi_n^{(0)} \rangle + \sum_{n \neq k}^{\infty} c_{nk} E_k^{(0)} \langle \phi_n^{(0)} | \phi_k^{(0)} \rangle = E_n^{(1)} \langle \phi_n^{(0)} | \phi_n^{(0)} \rangle + \sum_{n \neq k}^{\infty} c_{nk} E_n^{(0)} \langle \phi_n^{(0)} | \phi_k^{(0)} \rangle, \quad (2.15)$$

which tells us that

$$\boxed{E_n^{(1)} = \langle \phi_n^{(0)} | H' | \phi_n^{(0)} \rangle}, \quad (2.16)$$

which says the first order correction is the expectation value of the perturbation. So now if we multiply by $(\phi_l^{(0)})^*$ where $l \neq n$, we get that

$$\langle \phi_l^{(0)} | H' | \phi_n^{(0)} \rangle + c_{nl} E_l^{(0)} = E_n^{(1)} + c_{nl} E_n^{(0)}. \quad (2.17)$$

If we switch index for $l \rightarrow k$ for consistency, this gives us that

$$\boxed{c_{nk} = \frac{\langle \phi_k^{(0)} | H' | \phi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}}} \quad (2.18)$$

So if we examine the symmetries of the perturbing Hamiltonian, we get that the first order $n = 0$, the integral is equal to 0. High order terms do not contribute much, so we only really need to correct order 2. This makes good physical sense and gives us the first order solution.

So if we go to the next order, we get that

$$H_0 \phi_n^{(2)} + H' \phi_n^{(1)} = E_n^{(0)} \phi_n^{(2)} + E_n^{(1)} \phi_n^{(1)} + E_n^{(2)} \phi_n^{(0)}, \quad (2.19)$$

where

$$\phi_n^{(2)} = \sum_{k \neq n} c_{nk}^{(2)} \phi_k^{(0)}, \quad (2.20)$$

which upon substitution into the previous equation gives

$$H_0 \sum_{k \neq n} c_{nk}^{(2)} \phi_k^{(0)} + H' \sum_{k \neq n} c_{nk}^{(1)} \phi_k^{(0)} = E_n^{(0)} \sum_{k \neq n} c_{nk}^{(2)} \phi_k^{(0)} + E_n^{(1)} \sum_{k \neq n} c_{nk}^{(1)} \phi_k^{(0)} + E_n^{(2)} \phi_n^{(0)}. \quad (2.21)$$

Now if we multiply by $(\phi_n^{(0)})^*$ and integrate over all states, then we get

$$\sum_{k \neq n} c_{nk}^{(1)} \langle \phi_n^{(0)} | H' | \phi_k^{(0)} \rangle = E_n^{(2)} \quad (2.22)$$

which implies that

$$E_n^{(2)} = \sum_{k \neq n} \frac{\left| \langle \phi_k^{(0)} | H' | \phi_n^{(0)} \rangle \right|^2}{E_n^{(0)} - E_k^{(0)}} \quad (2.23)$$

If we let $n = 0$ be the lowest state then, we have that

$$E_0^{(2)} = \sum_{k > 0} \frac{\left| \langle \phi_k^{(0)} | H' | \phi_0^{(0)} \rangle \right|^2}{E_0^{(0)} - E_k^{(0)}}, \quad (2.24)$$

which implies that the second order perturbation correction to the ground state must be negative.

2.2 Variational Method

If we take some arbitrary function

$$\frac{\langle \psi(q) | \hat{H} | \psi(q) \rangle}{\langle \psi(q) | \psi(q) \rangle} = E_{var}, \quad (2.25)$$

then it can be shown that $E_{var} \geq E_0$. So the variation method sets an upper bound on the ground state energy. For example, if we take the quartic oscillator with $V = \frac{1}{2}k_4x^4$ and guess as a solution the harmonic oscillator

$$\psi(x) = Ne^{-\alpha x^2}, \quad (2.26)$$

then we will get that

$$\langle \psi(x) | H | \psi(x) \rangle = N^2 \int e^{-\alpha x^2} H e^{-\alpha x^2} dx, \quad (2.27)$$

which will give $E_{var}(\alpha, m, k_4)$. If we then find

$$\frac{\partial E_{var}}{\partial \alpha} \Big|_{k_4, m} = 0, \quad (2.28)$$

we find the upper bound. More systematically, we can expand this function in terms of a complete set of basis state, so we if we have ϕ which is the true state, but not known, we can expand in terms of $|1\rangle, |2\rangle, |3\rangle$

$$\phi(x) = \sum c_1 |1\rangle + c_2 |2\rangle + c_3 |3\rangle. \quad (2.29)$$

We know that the variational theorem guarantees that regardless of the coefficients, the normalized expectation value of the Hamiltonian, E_{var} , is greater than the ground state. So this means that

$$\frac{\partial E_{var}}{\partial c_1} = \frac{\partial E_{var}}{\partial c_2} = \frac{\partial E_{var}}{\partial c_3} = 0, \quad (2.30)$$

at the best possible solution. There are three coefficients, so we can generate a system of three linear homogeneous equations to solve for them. So we have that

$$\begin{aligned}
\langle \phi | H | \phi \rangle &= c_1 c_1 \langle 1 | H | 1 \rangle + c_1 c_2 \langle 1 | H | 2 \rangle + c_2 c_1 \langle 2 | H | 1 \rangle + c_2 c_2 \langle 2 | H | 2 \rangle + \dots \\
&= \sum_{i,j=1}^3 \langle \phi_i | H | \phi_j \rangle \\
&= c_{ij} H_{ij},
\end{aligned} \tag{2.31}$$

which we can write in matrix form as

$$\begin{pmatrix} c_1^2 H_{11} & c_1 c_2 H_{12} & c_1 c_3 H_{13} \\ c_2 c_1 H_{21} & c_2^2 H_{22} & c_2 c_3 H_{23} \\ c_3 c_1 H_{31} & c_3 c_2 H_{32} & c_3^2 H_{33} \end{pmatrix}, \tag{2.32}$$

and so if we define

$$S = \langle \phi | \phi \rangle, \tag{2.33}$$

and if the basis is orthogonal, then S will be a diagonal matrix. So we can take the derivative with respect to any of the parameters, for example

$$\frac{\partial}{\partial c_1} \left[\langle \phi | \phi \rangle E_{var} = \langle \phi | \hat{H} | \phi \rangle \right], \tag{2.34}$$

after application of the product rule and setting $\frac{\partial}{\partial c_1} E_{var} = 0$, we get the equation

$$2E_{var}[c_1 S_{11} + c_2 S_{12} + c_2 S_{21} + c_3 S_{13} + c_3 S_{31}] = 2[c_1 H_{11} + c_2 H_{12} + c_3 H_{13}], \tag{2.35}$$

and two more equations for c_2, c_3 . If we group all of the equations together, we can produce the matrix equation

$$\begin{pmatrix} H_{11} & H_{12} & H_{13} \\ H_{21} & H_{22} & H_{23} \\ H_{31} & H_{32} & H_{33} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = E_{var} \begin{pmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}, \tag{2.36}$$

of which there are 3 non-trivial solutions. We can always find general eigenvalues and in the case of an orthogonal basis, E_{var} is the eigenvalues of the H matrix since get the equation

$$(H - E1)c = 0. \tag{2.37}$$

So we will get E_i for $i = 1, 2, 3$, and we define a matrix C where the columns are the particular solution multiplied by a diagonal energy matrix

$$C = \begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix} \begin{pmatrix} E_1 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 \end{pmatrix}. \tag{2.38}$$

The C matrix must be orthogonal in sense that $CC^T = 1$ and this will give us orthogonal solution. So we can reach the final form of the problem by pre-multiplying both sides by C^T as

$$C^T H C = E. \tag{2.39}$$

So C is the transformation which diagonalizes H and gives the values for the energy in a diagonal matrix. In order to solve this, one would solve the secular determinant. This is given as

$$\begin{pmatrix} H_{11} - E & H_{21} \\ H_{12} & H_{22} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c - 2 \end{pmatrix} = 0, \quad (2.40)$$

which only has non-trivial solutions, when the determinant of the matrix is zero,

$$f(E) = (H_{11} - E)(H_{22} - E) - H_{12}^2 = 0. \quad (2.41)$$

In general, this will be a polynomial in E of order n , where n is the size of the matrix. This function $f(E)$ will be an upturning parabola whose zeros are the energies. This is the case where the overlap matrix S is a unit matrix. If we are in the general case, where S is not a unit matrix, we are solving the equation

$$HC = SCE, \quad (2.42)$$

and we need to solve the generalized eigenvalue problem. The other way to do this is to construct an orthogonal basis.

2.2.1 Constructioning Orthogonal Basis

The first method is Gram-Schmidt. The general principle is that we have

$$\langle \phi_i | \phi_j \rangle = S_{ij}, \quad (2.43)$$

where $S_{ii} = 1$, and we want to construct an orthogonal basis $\phi'_2 = A_2\phi_1 + B_2\phi_2$ such that

$$\langle \phi_1 | \phi'_2 \rangle = 0. \quad (2.44)$$

We also require ϕ'_2 to be normalized such that

$$\langle \phi'_2 | \phi'_2 \rangle = 1. \quad (2.45)$$

This gives rise to the following equations

$$\begin{cases} A_2 \langle \phi_1 | \phi_1 \rangle + B_2 \langle \phi_1 | \phi_2 \rangle &= A_2 + B_2 S_{12} = 0 \\ \langle \phi'_2 | \phi'_2 \rangle &= A_2^2 + B_2^2 + 2A_2 B_2 S_{12} = 1 \end{cases}, \quad (2.46)$$

which we can solve.

The second way to do this is to diagonalize S and renormalize. This consists of the following steps:

1. Diagonalize S .
2. Renormalize eigenvectors of S .
3. Transform H into new basis.
4. Diagonalize H .

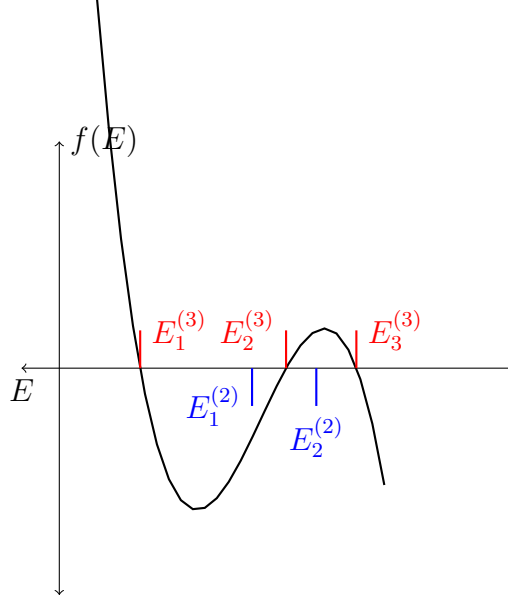


Figure 1: General cubic function with three roots.

2.2.2 Bounds on Higher Energy Level

We know that the linear variational method bounds the lowest energy level, we want to know how to bound higher energy levels. Lets assume that $n = 3$, this means we have a secular determinant of the following form

$$\begin{pmatrix} H_{11} - E & H_{12} & H_{13} \\ H_{21} & H_{22} - E & H_{23} \\ H_{31} & H_{32} & H_{33} - E \end{pmatrix}, \quad (2.47)$$

which gives rise to a cubic equation in E , which we denote $f(E)$. This function looks like a general cubic as in Figure 1. By knowing the energy levels $E_n^{(2)}$, we can form the determinant

$$f(E) = \begin{vmatrix} E_1^{(2)} - E & 0 & h_1 \\ 0 & E_2^{(2)} - E & h_2 \\ h_1 & h_2 & h_{33} - E \end{vmatrix} = 0, \quad (2.48)$$

which is a cubic function of E . So if we suppose that $E = E_1^{(2)}$, then we know can see that the general equation

$$f(E) = (E_1^{(2)} - E)(E_2^{(2)} - E)(h_{33} - E) - h_2^2(E_1^{(2)} - E) - h_1^2(E_2^{(2)} - E) \quad (2.49)$$

reduces to

$$f(E_1^{(2)}) = -h_1^2(E_2^{(2)} - E_1^{(2)}) < 0. \quad (2.50)$$

If we instead suppose that $E_1 = E_2^{(2)}$, then we get the following

$$f(E_2^{(2)}) = -h_2^2(E_1^{(2)} - E_2^{(2)}) > 0, \quad (2.51)$$

which implies that one of the roots must lie between these two points. We also know that

$$\lim_{E \rightarrow -\infty} f(E) = \infty; \quad \lim_{E \rightarrow \infty} f(E) = -\infty, \quad (2.52)$$

so we must have another root less than $E_1^{(2)}$ and $E_2^{(2)}$. So the point is that the ordering of the roots must be

$$\boxed{E_1^{(3)} \leq E_1^{(2)} \leq E_2^{(3)} \leq E_2^{(2)} \leq E_3^{(3)}}, \quad (2.53)$$

and in general, the roots interleave the previous n . So the first level is always lower than the previous n and the rest are in between the previous n .

In general, this may not be linear, such as when we have the function being Hermite polynomials as

$$\phi_n = H_n(x)e^{-\alpha x^2}, \quad (2.54)$$

and so we will need to curve fit α to get the best energy levels. It is okay to use different α for different n . It should probably be pretty close in practice.

3 Electronic Structure of Atoms

3.1 Hydrogenic Atoms

In a Hydrogen like atom, the potential depends only on r and usually given as

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}. \quad (3.1)$$

The Hamiltonian is then given as

$$H = -\frac{\hbar^2}{2\mu r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \hat{L}^2(\theta, \phi) \right] + V(r), \quad (3.2)$$

where \hat{L}^2 is the angular momentum operator and μ is the reduced mass given as

$$\mu = \frac{m_a m_b}{m_a + m_b}. \quad (3.3)$$

In the case of the hydrogen atom,

$$\mu_H = \frac{m_e m_{proton}}{m_e + m_{proton}} \approx m_e. \quad (3.4)$$

If we define distance in terms of the Bohr radius, give as

$$a_0 = \frac{4\pi\epsilon_0 \hbar}{m_e e^2}. \quad (3.5)$$

So if we now work in units of a_0 , where $r = r/a_0$. Then we have that

$$V(r) = \frac{-e^4 m_e Z}{(4\pi\epsilon_0)^2 \hbar^2 r}, \quad (3.6)$$

and we get the transformed kinetic energy as

$$H(r, \theta, \phi) = \frac{m_e e^4}{(4\pi\epsilon_0)^2 \hbar^2} \left[-\frac{1}{2r^2} \left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \hat{L}^2(\theta, \phi) \right) \right] \quad (3.7)$$

So we can write our Schrodinger equation as

$$\left[-\frac{1}{2r^2} \left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \hat{L}^2(\theta, \phi) \right) - \frac{Z}{r} \right] \psi(r, \theta, \phi) = \frac{(4\pi\epsilon_0)^2 \hbar^2}{m_e e^4} E \psi(r, \theta, \phi). \quad (3.8)$$

Normally, we measure in units of Hartree defined as

$$\epsilon = \frac{(4\pi\epsilon_0)^2 \hbar^2}{m_e e^4} E \quad (3.9)$$

So we can rewrite this equation as

$$\left[-\frac{d}{dr} r^2 \frac{d}{dr} - \hat{L}^2(\theta, \phi) - 2Zr \right] \psi(r, \theta, \phi) = Zr^2 \epsilon \psi(r, \theta, \phi), \quad (3.10)$$

which is a separable partial differential equation. So we can write the solution as a product

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi). \quad (3.11)$$

The rest of the solution is known and its derivation will not be repeated here. The solution to the Y component are the spherical harmonics, and the solutions to the R component are proportional to the Laguerre polynomials. In these units, the lowest energy is $-1/2$. If we are working with He^+ , then the lowest energy is given at -2 . The general expression is

$$\epsilon = -\frac{Z^2}{2n^2}. \quad (3.12)$$

So the dumbest guess for the energy of He is -4 , however it is really -2.9 due to pair repulsion. We will discuss this later.

Inside the expanded equations are a quantum number j relating to the \hat{L}^2 operator. It turns out that the energies are independent of j .

3.2 Spherical Box

Consider a spherical box where

$$V(r) = \begin{cases} 0 & 0 \leq r \leq a \\ \infty & r > a \end{cases}. \quad (3.13)$$

We can then write down a similiar equation to before in terms of $G(r) = rR(r)$, which reduces to

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{j(j+1)}{2r^2} \right] G(r) = \epsilon G(r). \quad (3.14)$$

when $j = 0$, this is just a particle in a box and

$$\psi(r) = \sqrt{\frac{2}{a}} \sin(kr), \quad (3.15)$$

where

$$k = \frac{n\pi}{a}. \quad (3.16)$$

when $j = 1$, we do not have as simple of an answer. However, we know that raising j will raise the energy. We can see this as a reduction of the effective particle in a box potential at each n .

3.3 Helium Atom

Helium has two electrons, so we can write the Hamiltonian as

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} = h(1) + h(2) + \frac{1}{r_{12}} \quad (3.17)$$

where $r_{12} = |r_1 - r_2|$. One thing to note is that the Hamiltonian is symmetric under exchange of particles. Implicitly we are working under the assumption that the nucleus is fixed. Of course, the nucleus is not fixed, and we will come back to this issue later. This is a general formula and we can write for N electrons

$$H(1, 2, \dots, N) = \sum_{i=1}^N h(i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{r_{ij}}. \quad (3.18)$$

This will also be true for molecules which we will see later. Now back to Helium. We can treat this as a perturbation problem with

$$H = \underbrace{h(1) + h(2)}_{H_0} + \underbrace{\frac{1}{r_{12}}}_{H_1}, \quad (3.19)$$

and since H_0 is separable, we can write

$$\psi(1, 2)_n^{(0)} = \phi(1)\phi(2); \epsilon_i = -\frac{Z^2}{2n_i^2}, \quad (3.20)$$

so if $n_1 = n_2 = 1$ then

$$E_0^{(0)} = -Z^2, \quad (3.21)$$

and

$$\psi_1^{(0)} = 1s(1)1s(2) = R(r_1)Y_{00}(\theta_1, \phi_1)R(r_2)Y_{00}(\theta_2, \phi_2). \quad (3.22)$$

Remember to keep everything normalized, if we do this then,

$$R(r_1)Y_{00}(\theta_1, \phi_1) = \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr}. \quad (3.23)$$

So now we want to find the correction to the zero order energy which in Hartree units is given as

$$E_1^{(0)} = -4. \quad (3.24)$$

So we can calculate

$$E_1^{(1)} = \int \psi_1^{(0)} H' \psi_1^{(0)} d\tau = \left(\frac{Z^3}{\pi}\right)^2 \int e^{-2Zr_1} \frac{1}{r_{12}} e^{-2Zr_2} r_1^2 r_2^2 \sin \theta_1 \sin \theta_2 dr_1 dr_2 d\theta_1 d\theta_2 d\phi_1 d\phi_2, \quad (3.25)$$

which has six degrees of freedom. We can then take

$$\frac{1}{r_{12}} = \frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{\lambda=0}^{\infty} \frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} P_{\lambda}(\cos \theta_{12}), \quad (3.26)$$

where

$$\theta_{12} = \cos^{-1} \left(\frac{\vec{r}_1 \cdot \vec{r}_2}{r_1 r_2} \right), \quad (3.27)$$

and $r_{<} = \min(r_1, r_2)$ and $r_{>} = \max(r_1, r_2)$. So we have expanded in the form of Legendre polynomials. This helps us because if we know that

$$\vec{r} = r(\cos \theta \hat{z} + \sin \theta \cos \phi \hat{x} + \sin \theta \sin \phi \hat{y}), \quad (3.28)$$

which implies that

$$\vec{r}_1 \cdot \vec{r}_2 = r_1 r_2 (\cos \theta_1 \cos \theta_2 + \sin \theta_1 \cos \phi_1 \sin \theta_2 \phi) + \dots, \quad (3.29)$$

which implies that $\cos \theta_{12}$ are the inner terms in the last equation. So if we integrate over any of these quantities, we are going to get zero. So the only term in the expression that will survive in the power series expansion is when $\lambda = 0$ such that there is a constant for $\cos \theta_{12}$. This has to do with the spherical symmetry of the ground state wavefunctions. Another way to say it is that all values of θ_{12} are equally probable.

So this makes it slightly easier since we can write

$$\frac{1}{r_{12}} = \frac{1}{r_{<}}, \quad (3.30)$$

since $P_0 = 1$. So we can write the integral as

$$(4\pi)^2 \left(\frac{Z^3}{\pi} \right)^2 \int_0^\infty \int_0^\infty e^{-2Zr_1} e^{-2Zr_2} \frac{1}{r_{>}} r_1^2 r_2^2 dr_1 dr_2 \quad (3.31)$$

Now we can break this apart into the correct terms to take account for the $r_{>}$ and we have

$$E_n^{(1)} = (4\pi)^2 \left(\frac{Z^3}{\pi} \right)^2 \int_0^\infty r_1^2 dr_1 \left[\int_0^{r_1} r_2^2 \frac{1}{r_1} e^{-2Z(r_1+r_2)} dr_2 + \int_{r_1}^\infty r_2 e^{-2Z(r_1+r_2)} dr_2 \right]. \quad (3.32)$$

This integral can be computed as $5Z/8$. So the energy up to first order winds up being

$$-4 + \frac{5Z}{8} = -2.75 (Z = 2). \quad (3.33)$$

One can measure this energy by measuring the ionization energy of He by putting it in an external field. We can find a threshold and this is the ionization potential. We will also find another ionization potential for He^{2+} . If we add these two ionization potentials, we get the ground energy. We can also stop at the first step and realize we then have a hydrogenic atom and say that $E(He) = -2 - IP$, where IP is the ionization potential and is positive by convention. This gives us about $IP = 0.904$. We calculate 0.75 . This is not great agreement. So we can do second order perturbation theory, but it would be really complicated because we would need to include all the excited states and all the continuum states. So the better way is to do the variational method and make Z a variable parameter in the wavefunction to account for nuclear shielding. So we can write

$$E_{var}(\zeta) = 2 \langle h(1) \rangle + \left\langle \frac{1}{r_{12}} \right\rangle = \frac{\zeta^3}{\pi} \int e^{-\zeta r} \left[-\frac{1}{2} \nabla_r^2 - \frac{Z}{r} \right] e^{-\zeta r} r^2 \sin \theta dr d\theta d\phi + \frac{5\zeta}{8} \quad (3.34)$$

We can write two electron integrals in a compact way by writing

$$[1s^2|1s^2], \quad (3.35)$$

where the bar stands for $1/r_{12}$ and the $1s^2$ are electron wavefunctions. After some calculations which will be done on the homework, we can find the final variations energy as

$$\langle H \rangle = \frac{5}{8}\zeta + 2 \left(-Z\zeta + \frac{\zeta^2}{2} \right) = E_{var}(\zeta), \quad (3.36)$$

which we can minimize by saying that

$$\frac{\partial E_{var}}{\partial \zeta} = \frac{5}{8} - 2Z + 2\zeta = 0, \quad (3.37)$$

which gives us that $\zeta = 27/16$ at the minimum (for He). Plugging this in, the energy turns out to be -2.8475 , which is still quite different from -2.9 , the measured value. We can choose something more general for the $1s$ function which leads us to the Hartree-Fock method.

3.4 Hartree-Fock (Mean Field Theory)

Suppose we say the wavefunction is given as

$$\psi(1, 2) = 1s(1)1s(2) = \phi(1)\phi(2), \quad (3.38)$$

and we want to find the best ϕ . So we need to solve some Schrodinger equation

$$\hat{h}\phi = \epsilon\phi, \quad (3.39)$$

where the Hamiltonian is modified as

$$\hat{h} = -\frac{1}{2}\nabla^2 - \frac{Z}{r_1} + \int \phi(2) \frac{1}{r_{12}} \phi(2) dv_2, \quad (3.40)$$

where the last term is the mean field of the other electron, which is really some function $f(r_1)$. This cannot be solved analytically, we need some sort of iterative numeric procedure. It works like this:

1. Choose $\phi(r)$.
2. Calculate $\int \phi^2(r_2) \frac{1}{r_{12}} dr_2$
3. Solve 1 electron equation for $\phi(r_1)$.
4. Solve 1 electron equation for $\phi(r_2)$.
5. Iterate until it converges (hopefully).

So now we have obtained ϵ , we can relate this to the atom. For the He atom, we get $\epsilon = -.9179$. We know that

$$\epsilon = \langle \phi | h | \phi \rangle = \langle \phi | h(1) | \phi \rangle + \int \phi(1)^2 dV_1 \int \phi(2)^2 \frac{1}{r_{12}} dV_2. \quad (3.41)$$

So we know that

$$2\epsilon = 2\text{electron energy} + 2[\phi^2|\phi^2], \quad (3.42)$$

so the actual energy is

$$E = 2\epsilon - [1s^2|1s^2], \quad (3.43)$$

which in the case of the He atom is -2.8618 . This is not much different than our previous result which says that the initial guess in our variational method is pretty good. However, this model is missing electron correlation. This is a very complicated thing to solve, however, there is a correlation energy which is defined as

$$E_{CE} = E_{HF} - E_{true}. \quad (3.44)$$

So we want to know how to calculate this. The idea is to include electron excitations and add terms in the form of $\phi(1)2s(2) + \dots$ to the wavefunctions and also consider multiple electron excitations. The Hartree-Fock is stable to the one electron excitations, but the two electron excitations influence the result. So we will consider the wavefunction

$$\psi = C_{1s^2}1s(1)1s(2) + C_{2p_z^2}2p_z(1)2p_z(2) \quad (3.45)$$

So now we can calculate

$$\langle\psi|H|\psi\rangle = \begin{pmatrix} \langle 1s^2|H|1s^2\rangle & \langle 1s^2|H|2p_z^2\rangle \\ \langle 2p_z^2|H|1s^2\rangle & \langle 2p_z^2|H|2p_z^2\rangle \end{pmatrix} \quad (3.46)$$

Now we can notice that the off diagonal terms will only contain terms of the form $[1s^2|2p_z^2]$ since the wavefunction overlap will vanish due to the orthogonality of Legendre polynomials. By diagonalizing this matrix, we will get a better approximation to the energy. We can think of this physically by considering orbitals

$$\chi_+ = 1s + \delta 2p_z; \chi_- = 1s - \delta 2p_z, \quad (3.47)$$

which will qualitatively keep the electrons out of each others way. So if we consider

$$\psi(1,2) = \chi_+(1)\chi_-(2) + \chi_-(1)\chi_+(2), \quad (3.48)$$

where the second term comes from indistinguishability in quantum mechanics. Plugging in the definitions of ψ gives us cross terms which will vanish, giving us

$$\psi(1,2) = 1s(1)1s(2) - \delta^2 2p_z(1)2p_z(2), \quad (3.49)$$

which is exactly the same as our matrix formulation. By including these excitations, we can get arbitrarily close to the exact energy. A great thing about this method is that it is systematically improvable by including more terms.

3.4.1 Basis Set

Now we will discuss how to numerically solve a problem like

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + V(r) \right] \phi(r) = E\phi(r). \quad (3.50)$$

The approach is to calculate the second derivative on a discrete grid of points. So if consider a function f evaluate at points x_i such that $f(x_i) = f_i$, and $x_i - x_{i-1} = h$, then we can rewrite this equation as

$$-\frac{1}{2h^2} [f_1 + f_3 - 2f_2] + V_2 f_2 = E f_2, \quad (3.51)$$

by using approximations that become exact as $h \rightarrow 0$. We also know that the logarithmic derivative defined as

$$\frac{d}{dx} \ln f(x) = \frac{1}{f} \frac{df}{dx}, \quad (3.52)$$

is continuous. So we can approach the wavefunction from both sides and see if it is the same in the middle by guessing an energy. We can then adjust until we have the solution.

In practice these grid methods only really work for one dimension. So for higher dimensional problems, we choose a basis and expand in a basis, such as a ζ basis

$$c_1 e^{-\zeta_1 r} + c_2 e^{-\zeta_2 r} + c_e e^{-\zeta_3 r} + \dots \quad (3.53)$$

We then solve the secular equation and find the lowest energy eigenstate and then iterate and minimize. So we will obtain a bunch of virtual orbitals which are not occupied with correspond with the two electron excitations. In He, we can keep adding virtual orbitals and we will slowly converge to the answer. The slowness comes from the fact that the virtual orbitals are uncorrelated functions which means that they say the maximal probability is finding the two electrons at exactly the same place, even though we know this is very unlikely since electrons repel each other.

In larger atoms, this becomes very difficult. Take Be which has electron configuration $1s^2 2s^2$. We would need to solve for simultaneous solutions. It is possible and results in a large matrix equation.

3.5 Spin States

We have not included a description of the spin of the electrons at this point. So we need to add a wavefunction $|S(1, 2)\rangle$. So we know that

$$S|1, 2\rangle = \sum |(m_{s_1})|m_{s_2}\rangle. \quad (3.54)$$

We know that $M_s = 1, 0, -1$, since $M = m_1 + m_2$ by the rules of vector addition and so we can write

$$|S = 1, M_s = 1\rangle = |+, +\rangle |S = 1, M_s = -1\rangle = |-, -\rangle, \quad (3.55)$$

however for $M = 0$, we have two possible states which work $|+, -\rangle, |-, +\rangle$. Since the Hamiltonian is symmetric under exchange, the wavefunction must also be symmetric and so we need to use linear combinations of these two products

$$|S = 1, M_s = 0\rangle = \frac{1}{\sqrt{2}}(|+, -\rangle + |-, +\rangle). \quad (3.56)$$

We can also get this by using the lowering operator defined as

$$J_- |j, m\rangle = \sqrt{j(j+1) - m(m-1)} |j, m-1\rangle, \quad (3.57)$$

so we know that

$$S_- |1, 1\rangle = \sqrt{2} |10\rangle \quad (3.58)$$

We know that the two spin operator is $S_- = S_{1-} + S_{2-}$. Knowing the eigenvalues of S_1, S_2 has magnitude $1/2$. We can operate

$$S_- |++\rangle = \sqrt{\frac{1}{2} \frac{3}{2} - \frac{1}{2} \frac{1}{2}} (|- , +\rangle + |+ , -\rangle) = |- , +\rangle + |+ , -\rangle, \quad (3.59)$$

and so if we divide both sides by the factor of $\sqrt{2}$, we get our result. We have one other state

$$|0, 0\rangle = \frac{1}{\sqrt{2}} (|+ , -\rangle - |- , +\rangle) \quad (3.60)$$

3.6 Excited States of He

3.6.1 Symmetry Considerations

We know that the ground state of He is $1s(1)1s(2)$, so we know that for the ground state

$$\psi(1, 2) = 1s(1)1s(2) |S, M_s\rangle, \quad (3.61)$$

and so if we define a permutation operator

$$\hat{P}_{12} f(1, 2) = f(2, 1), \quad (3.62)$$

since this operator commutes with the Hamiltonian, we know that

$$\hat{P}_{12} f(1, 2) = \pm f(1, 2) \quad (3.63)$$

and so for an electron which is a fermion

$$f(2, 1) = -f(1, 2). \quad (3.64)$$

So we know that

$$\hat{P}_{12} \psi(1, 2) = \hat{P}_{12} 1s(1)1s(2) |S, M_s\rangle = 1s(2)1s(1) P_{12} |S, M_s\rangle, \quad (3.65)$$

and so the spin function must be antisymmetric since the s functions are symmetric. This is called the singlet state. So we must use the antisymmetric spin wavefunction $|S = 0, M_s = 0\rangle$. From this comes the Pauli exclusion principle.

3.6.2 Energy Calculation

For the excited state, we can write the wavefunction as the $s = 0$ state

$$\psi = \frac{1}{\sqrt{2}} [1s(1)2p(2) + 1s(2)^2 p(1)] \frac{1}{\sqrt{2}} [|+ , 0\rangle - - , +], \quad (3.66)$$

or the $S = 1$ states

$$\frac{1}{\sqrt{2}} [1s(1)2p(2) - 1s(2)^2 p(1)] |+ , +\rangle \quad (3.67)$$

$$\frac{1}{\sqrt{2}} [1s(1)2p(2) - 1s(2)^2 p(1)] \frac{1}{\sqrt{2}} [|+ , 0\rangle + - , +] \quad (3.68)$$

$$\frac{1}{\sqrt{2}} [1s(1)2p(2) - 1s(2)^2 p(1)] |- , 0\rangle. \quad (3.69)$$

Now we can find the energy. The Hamiltonian has not changed and can still be written as

$$H(1, 2) = h(1) + h(2) + \frac{1}{r_{12}}, \quad (3.70)$$

so

$$\langle \psi | H | \psi \rangle = \int \psi^* H(1, 2) dV_1 dV_2 ds_1 ds_2 \psi, \quad (3.71)$$

which leads to 16 terms, however, many of the spins terms will be zero. The off diagonal surviving terms all have the pattern

$$\int 1s(1)2p(2)H1s(1)2p(2); \in \int 1s(2)2p(1)H1s(2)2p(2), \quad (3.72)$$

with some spin functions, which will give us two times either one. So the diagonal terms will look like

$$\langle 1s|h|1s \rangle + \langle 2p|h|2p \rangle + \int 1s^2(1)\frac{1}{r_{12}}2p^2(2)dV_1dV_2, \quad (3.73)$$

where the third term corresponds to the average interaction between an electron in the $2s$ orbital and an electron in the $2p$ orbital, which we can write as $[1s^2|2p^2]$. Then we will have off diagonal terms which have no contribution from the orthogonal one electron terms, and so they have form

$$[1s2p|2p1s], \quad (3.74)$$

which is an overlap charge density of some multiplication of orbitals. In this case it is kind of the self energy. This is non-classical because it only results from the inclusion of Fermi-Dirac statistics and the requirement of anti-symmetry. For the singlet state this will be a positive contribution and for the triplet states this term will be a negative contribution. So the net result is that the energy is given as

$$\langle 1s|h|1s \rangle + \langle 2p|h|2p \rangle + [1s^2|2p^2] \pm [1s2p|2p1s], \quad (3.75)$$

where the triplet is the lower state. Sometimes the term $[1s2p|2p1s]$ is called an exchange integral, and the spacing is twice this term. Notice that there is zero probability in the triplet state that the electrons are in the same place, whereas there is in the singlet state. So in the triplet state, the average repulsion is smaller and the energy is lower.

As we go to higher state, the splitting gets smaller since the overlap integrals decrease.

3.7 Multi-Electron Atoms

For more than two electrons, we cannot separate the spacial and spin parts of the wavefunction. However, there is a nice way of writing the wavefunction as a Slater determinant. In order to introduce this we need to introduce the concept of a spin-orbital which is the product of an orbital and an spin. In this case we will use the notation $1s(1), \overline{1s}(1)$, where the bar stands for spin down and no bar for spin up.

3.7.1 Slater Determinant

So when we need anti-symmetry, we can write

$$\frac{1}{\sqrt{2}}[1s(1)\overline{1s}(2) - \overline{1s}(1)1s(2)] = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1) & \overline{1s}(1) \\ 1s(2) & \overline{1s}(2) \end{vmatrix} \quad (3.76)$$

For Li, we have 3 spin-orbitals $1s, \overline{1s}, 2s$. So we can write the wavefunction as

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} 1s(1) & \overline{1s}(1) & 2s(1) \\ 1s(2) & \overline{1s}(2) & 2s(2) \\ 1s(3) & \overline{1s}(3) & 2s(3) \end{vmatrix}, \quad (3.77)$$

where N is the number of electrons. Notice the columns are spin orbitals and rows are electrons. Notice that interchange of electrons permutes the rows of the determinant which changes the sign of the function as desired. This particular determinant will yield six terms, so when we evaluate the $\langle \psi | H | \psi \rangle$ there will be 36 terms in the integral. Note that

$$H(1, 2, 3) = h(1) + h(2) + h(3) + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}. \quad (3.78)$$

In general, if one has a Slater determinant which contains spin orbits ϕ_1, \dots, ϕ_N , then the Slater determinant looks like

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \dots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \dots & \phi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(N) & \phi_2(N) & \dots & \phi_N(N) \end{vmatrix} \quad (3.79)$$

So if we write the Hamiltonian as

$$H = \sum_{i=1}^N h(i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{r_{ij}}, \quad (3.80)$$

then

$$\langle \psi | H | \psi \rangle = \sum_{i=1}^N \langle \phi_i | h | \phi_i \rangle + \sum_{i=1}^{N-1} \sum_{j=i+1}^N [\phi_i^2 | \phi_j^2] - \sum_{i=1}^{N-1} \sum_{j=i+1}^N \delta_{m_{J_i}, m_{J_j}} [\phi_i \phi_j | \phi_j \phi_i]. \quad (3.81)$$

We can write the Slater determinant as $|\phi_1 \phi_2 \dots \phi_N|$.

3.7.2 Be

Be is $N = 4$, so we have the wavefunction as $|1s\overline{1s}2s\overline{2s}|$. We know the Hamiltonian is

$$H = h(1) + h(2) + h(3) + h(4) + \frac{1}{r_{12}} + \dots + \frac{1}{r_{34}}, \quad (3.82)$$

where there are six $1/r$ terms. So the energy is

$$E = 2 \langle 1s | h | 1s \rangle + 2 \langle 2s | h | 2s \rangle + [1s^2 | 1s^2] + [2s^2 | 2s^2] + 4[1s^2 | 2s^2] - 2[1s2s | 2s1s]. \quad (3.83)$$

3.7.3 Carbon

The electronic structure is $1s^2 2s^2 2p^2$ where our p states are given as p_0, p_1, p_{-1} and the corresponding p with spin down. So we can write a Tableau table with m_L on the top and M_S on the left with ordering highest to lowest starting at the top left and get Table 1. So once we do this we determine that the possible states are $^1D, ^3P, ^1S$. We can use this in conjunction with Hund's rule, which says that the state with largest S is lowest and the state with largest L is next. So for carbon the lowest state is 3P , then 1D , then 1S .

	2	1	0	-1	-2
1		$p_1 p_0$	$p_1 p_{-1}$	$p_{-1} p_0$	
0	$p_1 \bar{p}_1$	$p_1 p_0; \bar{p}_1 p_0$	$p_0 \bar{p}_0; p_1 \bar{p}_{-1}; \bar{p}_1 p_{-1}$	$p_1 \bar{p}_0; \bar{p}_{-1} p_0$	$p_{-1} \bar{p}_{-1}$
-1		$\bar{p}_1 \bar{p}_0$	$\bar{p}_1 \bar{p}_{-1}$	$\bar{p}_{-1} \bar{p}_0$	

Table 1: Tableau method to count possible electron configurations.

To actually calculate the energy, we need to write down the Slater determinant

$$|1s\bar{1}s2s\bar{2}s2p_1\bar{2}p_1|. \quad (3.84)$$

We can switch basis, $|p_1\bar{p}_1\rangle = |LM_L SM_S\rangle = |2200\rangle$. So we have the following states

$$\begin{aligned}
|2, 2, 0, 0\rangle &= |p_1\bar{p}_1\rangle \\
|2, 1, 0, 0\rangle &= \frac{1}{\sqrt{2}} (|p_1\bar{p}_0\rangle + |p_0\bar{p}_1\rangle) \\
|2, 0, 0, 0\rangle &= \frac{1}{\sqrt{6}} (2|p_0\bar{p}_0\rangle + |p_1\bar{p}_{-1}\rangle + |p_{-1}\bar{p}_0\rangle) \\
|2, -1, 0, 0\rangle &= \frac{1}{\sqrt{2}} (|p_{-1}\bar{p}_0\rangle + |p_0\bar{p}_{-1}\rangle) \\
|1, 1, 1, 1\rangle &= |p_1 p_0\rangle \\
|1, 0, 1, 1\rangle &= \underbrace{|p_0 p_0\rangle}_{\text{not possible}} + |p_1 p_{-1}\rangle \\
|1, -1, 1, 1\rangle &= |p_0 p_{-1}\rangle \\
|1, 1, 1, -1\rangle &= |\bar{p}_1 \bar{p}_0\rangle \\
|1, 0, 1, -1\rangle &= |\bar{p}_1 \bar{p}_{-1}\rangle \\
|1, -1, 1, -1\rangle &= |\bar{p}_0 \bar{p}_{-1}\rangle \\
|1, 1, 1, 0\rangle &= \frac{1}{\sqrt{2}} (|\bar{p}_1 p_0\rangle + |p_2 \bar{p}_0\rangle) \\
|1, 1, 1, -1\rangle &= |\bar{p}_1 \bar{p}_0\rangle \\
|1, -1, 1, 1\rangle &= |p_{-1} p_0\rangle \\
|1, -1, 1, 0\rangle &= \frac{1}{\sqrt{2}} (|p_{-1} \bar{p}_0\rangle + |\bar{p}_{-1} p_0\rangle) \\
|1, -1, 1, -1\rangle &= |\bar{p}_{-1} \bar{p}_0\rangle.
\end{aligned} \quad (3.85)$$

Here there are nine triplet P states, triplet D states, and S states, which we can designate $|0, 0, 0, 0\rangle$ which will be

$$|0, 0, 0, 0\rangle = a|p_0\bar{p}_0\rangle + b|p_1\bar{p}_{-1}\rangle + c|p_{-1}\bar{p}_1\rangle \quad (3.86)$$

where the necessary factors a, b, c come from the orthogonality conditions and normalization. We can get that $a = b = 1/\sqrt{3}$ and $c = -1/\sqrt{3}$. So now we have constructed all the states. So now

we can calculate energy as

$$\begin{aligned}
& \left\langle \sum_{i=1}^6 h(i) + \sum_{i=1}^5 \sum_{j=2}^6 \frac{1}{r_{ij}} \right\rangle \\
&= 2 \langle 1s|h|1s \rangle + 2 \langle 2s|h|2s \rangle + 2 \langle 2p|h|2p \rangle \\
&+ [1s^2|1s^2] + [2s^2|2s^2] + 4[1s^2|1s^2] + 4[1s^2|2p^2] + 4[2s^2|2p^2] + [2p^2|2p^2] \\
&- 2[1s2s|2s1s] - 2[1s2p|2p1s] - 2[2s2p|2p2s]
\end{aligned} \tag{3.87}$$

where $[2p^2|2p^2]$ depends on the orbital. What differentiates the states is the expectation value of $1/r_{12}$. This will be easier to do if we use Cartesian p orbitals. We can write

$$2p_m = Y_{1,m}(\theta, \phi) r f(r), \tag{3.88}$$

and so for $m = 0$, we have that

$$2p_0 = r \cos \theta f(r) = z f(r). \tag{3.89}$$

We can also write

$$2p_1 = \frac{-1}{\sqrt{2}}(2p_x + 2ip_y) \tag{3.90}$$

$$2p_{-1} = \frac{1}{\sqrt{2}}(2p_x - 2ip_y). \tag{3.91}$$

We can now use this to write the determinants in terms of the Cartesian orbitals. First note that since the Hamiltonian is spherically symmetric, any rotation commutes with the Hamiltonian. This means that the angular momentum projection doesn't matter in this basic case since there is no preferred z axis, (this would be not true in an external field). So we can write

$$\begin{aligned}
\langle {}^1D_{20}|H|{}^1D_{20} \rangle &= |p_1 \overline{p_1}| \\
&= \frac{1}{2} [|p_x + ip_y)(\overline{p_x} + \overline{ip_y})] \\
&= \frac{1}{2} [|p_x \overline{p_x}| - |p_y \overline{p_y}| + i|p_x \overline{p_y}| + i|p_y \overline{p_x}|].
\end{aligned} \tag{3.92}$$

where we have used the identity

$$\det \begin{bmatrix} a+b & e \\ c+d & f \end{bmatrix} = \det \begin{bmatrix} a & e \\ c & f \end{bmatrix} + \det \begin{bmatrix} b & e \\ d & f \end{bmatrix} \tag{3.93}$$

And if we take linear combinations of these states, we get

$${}^1D_{x^2-y^2} = \frac{1}{\sqrt{2}}(|{}^2D_{20}\rangle + |{}^1D_{-20}\rangle) = \frac{1}{\sqrt{2}}[|p_x \overline{p_x}| - |p_y \overline{p_y}|], \tag{3.94}$$

and

$${}^1D_{xy} = \frac{-i}{\sqrt{2}}(|{}^2D_{20}\rangle - |{}^1D_{-20}\rangle) = \frac{1}{\sqrt{2}}[|p_x \overline{p_y}| + |p_y \overline{p_x}|], \tag{3.95}$$

which are both real, and so we can more easily calculate

$$\begin{aligned} \left\langle {}^1D_{x^2-y^2} \left| \frac{1}{r_{12}} \right|^1 D_{x^2-y^2} \right\rangle &= \frac{1}{2}([p_x^2|p_x^2] + [p_y^2|p_y^2] - 2[p_x p_y|p_y p_x]) \\ &= [p_x^2|p_x^2] - [p_x p_y|p_y p_x], \end{aligned} \quad (3.96)$$

where we have used the symmetry of p_x and p_y . So now we can look at

$$\begin{aligned} \left\langle {}^1D_{xy} \left| \frac{1}{r_{12}} \right|^1 D_{xy} \right\rangle &= \frac{1}{2}([p_x^2|p_y^2] + [p_y^2|p_x^2] + 2[p_x p_y|p_y p_x]) \\ &= [p_x^2|p_y^2] + [p_x p_y|p_y p_x], \end{aligned} \quad (3.97)$$

yet we know that

$$\left\langle {}^1D_{x^2-y^2} \left| \frac{1}{r_{12}} \right|^1 D_{x^2-y^2} \right\rangle = \left\langle {}^1D_{xy} \left| \frac{1}{r_{12}} \right|^1 D_{xy} \right\rangle, \quad (3.98)$$

which implies that

$$[p_x^2|p_x^2] - [p_x p_y|p_y p_x] = [p_x^2|p_y^2] + [p_x p_y|p_y p_x], \quad (3.99)$$

and we can solve to get

$$[p_x^2|p_x^2] = [p_x^2|p_y^2] + 2[p_x p_y|p_y p_x]. \quad (3.100)$$

Now we can look at the other states. We start with

$$|^3P_{00}\rangle = \frac{1}{\sqrt{2}}[|p_1\bar{p}_{-1}| - |p_{-1}\bar{p}_1|]. \quad (3.101)$$

We can write this in Cartesian orbitals as

$$\frac{i}{\sqrt{2}}(|p_x\bar{p}_y| - |p_y\bar{p}_x|), \quad (3.102)$$

and so we can write

$$\left\langle {}^3P_{00} \left| \frac{1}{r_{12}} \right|^3 P_{00} \right\rangle = [p_x^2|p_y^2] - [p_x p_y|p_y p_x], \quad (3.103)$$

which demonstrates Hund's rule that the triplet state is lower in energy and splitting between the singlet and the triplet state is given as $2[p_x p_y|p_y p_x]$. Now we will move on to singlet s , which is given as

$$|^1S_{00}\rangle = \frac{1}{\sqrt{3}}[|p_1\bar{p}_{-1}| + |p_{-1}\bar{p}_1| - |p_0\bar{p}_0|], \quad (3.104)$$

which we can write in terms of Cartesian coordinates as

$$\frac{-1}{\sqrt{3}}(|p_x\bar{p}_x| + |p_y\bar{p}_y| + |p_z\bar{p}_z|), \quad (3.105)$$

which has the proper spherical symmetry for an S orbital. So we have that

$$\left\langle {}^1S_{00} \left| \frac{1}{r_{12}} \right|^1 S_{00} \right\rangle = \frac{1}{3}([p_x^2|p_x^2] + [p_y^2|p_y^2] + [p_z^2|p_z^2] + 2[p_x p_y|p_y p_x] + 2[p_x p_z|p_z p_x] + 2[p_y p_z|p_z p_y]), \quad (3.106)$$

and if we use symmetry, we get

$$\left\langle {}^1S_{00} \left| \frac{1}{r_{12}} \right| {}^1S_{00} \right\rangle = [p_x^2 | p_x^2] + 2[p_x p_y | p_y p_x], \quad (3.107)$$

and so we see that this is the highest state and the splitting between the S and D states is $3[p_x p_y | p_y p_x]$. So the ratio of splitting between S and D to D and P should be $1.5/1$, however the theoretical splitting is more like $1.2/1$. This is not that bad considering we did no numerical calculations.

4 Molecular Electronic Structure

4.1 Dihydrogen Ion

4.1.1 Qualitative Overview

First we will study H_2^+ , for which we can write the electronic Hamiltonian as

$$H_{el} = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b}, \quad (4.1)$$

and the nuclear Hamiltonian as

$$H_{nuc} = -\frac{1}{2m_H}\nabla_{R_A}^2 - \frac{1}{2m_H}\nabla_{R_B}^2 + \frac{1}{R}, \quad (4.2)$$

where R is the distance between the nuclei, and the total Hamiltonian is

$$H = H_{el} + H_{nuc} \quad (4.3)$$

Now note that as $r \rightarrow \infty$ (separated atom limit), this becomes $H + H^+$ and so the electronic energies become that of a Hydrogen atom. As $r \rightarrow 0$ (united atom limit), the energies of the electron becomes a hydrogenic atom with $Z = 2$. So the electronic energy states must have a smooth line as a function of r . In this case, they must vary between $-1/2$ the separated limit and -2 at the united limit. When we add on the nuclear energy, this will diverge at $R = 0$. So we can find R_e the equilibrium distance as the minimum of this energy, and the distance between $E(R_e)$ and the separated atom limit is the dissociation energy D_e . This is order of magnitude 10 eV which is about a third of a Hartree.

4.1.2 Calculation

We write the total Hamiltonian as

$$H(\vec{r}, \vec{R}_A, \vec{R}_B) = H_{el}(\vec{r}; R) - \frac{1}{2m_H}\nabla_{R_A}^2 - \frac{1}{2m_H}\nabla_{R_B}^2 + \frac{Z_A Z_B}{R}. \quad (4.4)$$

Now we want to look for a wavefunction satisfying the Schrodinger equation

$$H(r, R)\Psi(r, R) = E\Psi(r, R), \quad (4.5)$$

where r, R are understood to be vectors. So note that we can write

$$-\frac{1}{2m_H}\nabla_{R_A}^2 - \frac{1}{2m_H}\nabla_{R_B}^2 = -\frac{1}{2M}\nabla_{R_{cm}}^2 - \frac{1}{2\mu}\nabla_R^2, \quad (4.6)$$

where μ is the reduced mass and

$$\vec{R}_{cm} = \frac{m_A\vec{R}_A + m_B\vec{R}_B}{m_A + m_B}, \quad (4.7)$$

and we can now only consider the center of mass coordinates. We know that any function can be expanded as a set of linear function and we will use the functions that solve

$$H_{el}(r, R)\phi_{el}^{(k)}(r, R) = \epsilon_{el}^{(k)}(R)\phi_{el}^{(k)}(r, R). \quad (4.8)$$

So we can write

$$\Phi(r, R) = \sum_k c_k(R)\phi_{el}^{(k)}(r, R). \quad (4.9)$$

Then we will pre-multiply by $\phi_{el}^{(l)}$ and integrate over the internal degrees of freedom (r) which will give a set of linear differential equations for the c_k . So we can write the Shrodinger equation as

$$\begin{aligned} & \left(H_{el} - \frac{1}{2\mu}\nabla_R^2 + \frac{Z_A Z_B}{R} \right) \sum_k c_k(R)\phi_{el}^{(k)}(r, R) \\ &= \sum_k c_k(R)H_{el}(r, R)\phi_{el}^{(k)}(r, R) - \frac{1}{r\mu} \sum_k \nabla_R^2 c_k(R)\phi_{el}^{(k)}(r, R) + \sum_k \frac{Z_A Z_B}{R} c_k(R)\phi_{el}^{(k)}(r, R) \\ &= \sum_k c_k(R)\epsilon_{el}^{(k)}(R)\phi_{el}^{(k)}(r, R) - \frac{1}{r\mu} \sum_k \nabla_R^2 c_k(R)\phi_{el}^{(k)}(r, R) + \sum_k \frac{Z_A Z_B}{R} c_k(R)\phi_{el}^{(k)}(r, R) \\ &= E \sum_k c_k(R)\phi_{el}^{(k)}(r, R) \end{aligned} \quad (4.10)$$

If we pre- multiply by $\phi_{el}^{(l)}$, and neglecting turns other than second order differential in c_k for the Laplacian operator (Born-Oppenheimer approximation), we get

$$c_l(R)\epsilon_{el}^{l(R)} - \frac{1}{2\mu}\nabla_R^2 c_l(R) + \frac{Z_A Z_B}{R} c_l(R) = E c_l(R), \quad (4.11)$$

which we can rearrange as

$$\left[\epsilon_{el}^{l(R)} - \frac{1}{2\mu}\nabla_R^2 + \frac{Z_A Z_B}{R} \right] c_l(R) = E c_l(R) \quad (4.12)$$

which itself is a Schrodinger equation with some effective potential only depending on R , $V^{(l)}(R)$. Note we have neglected terms, however in this approximation, we can solve this problem much more easily. Both of these terms involve derivatives of $\phi_{el}(r, R)$ which are generally very small. This approximation works as long as there is not much degeneracy between electronic states.

We have quantum number m_l of angular momentum, and we can label the states as σ for $m = 0$, π for $m = \pm 1$, and δ for $m = \pm 2$. We can then write the wavefunction as

$$\phi_{el}^{(k)}(r, R) = e^{\pm im\phi} f(r_a, r_b), \quad (4.13)$$

where r_a, r_b are the coordinates from the atoms to the nucleus. So we can write these functions as

$$\phi_{el}^{k=1}(r, R = \infty) = N(1s_a + 1s_b), \quad (4.14)$$

the sum of two one atomic wavefunctions, since the particles at infinity don't interact. We know that

$$\langle \phi_{el}^{(k)} | \phi_{el}^{(k)} \rangle = 1, \quad (4.15)$$

which implies that

$$\begin{aligned} 1 &= \int (\phi_{el}^{(k)})^2 dV \\ &= N^2 \int (1s_a + 1s_b)^2 dV \\ &= N^2 \left[\int 1s_a^2 dV + \int 1s_b^2 dv + 2S(R) \right] \\ &= 2N^2 [1 + S(R)]. \end{aligned} \quad (4.16)$$

where $S(R)$ is the overlap integral defined as $\int 1s_a 1s_b dv$ which is zero at infinity. So we get that

$$N = \frac{1}{\sqrt{2(1 \pm S(R))}} \quad (4.17)$$

So we get that

$$\phi_{el}^{\pm}(R) = \frac{1}{\sqrt{2(1 \pm S(R))}} (1s_a \pm 1s_b) \quad (4.18)$$

We also know the wavefunction for $R = 0$, which is the $1s$ wavefunction for the He^+ ion. So this is given as

$$\phi_{el}^{(k=1)} = \sqrt{\frac{8}{\pi}} e^{-2r}. \quad (4.19)$$

Now we can use the variational principle to calculate the electronic energy at each point. Then we can check it matches at the endpoints. We have calculated the energy as a function of the screening constant to be

$$E = \frac{1}{2}\zeta^2 - Z\zeta, \quad (4.20)$$

and for $\zeta = 1$, we have -1.5 at $R = 0$. This means that the approximation gets worse as $R \rightarrow 0$. So we can now let $\zeta(R)$ be a function of R and minimize at every point. This will give a better approximation. So we want to evaluate (assuming normalized wavefunctions)

$$\begin{aligned} \int \phi_{el}^{(k)} H_{el} \phi_{el}^{(k)} dV &= \frac{1}{2(1 + S)} \left[2 \int 1s_a \left(-\frac{1}{2} \nabla^2 \right) 1s_a + 2 \int 1s_a \left(-\frac{1}{2} \nabla^2 \right) 1s_b \right. \\ &\quad + \int 1s_a \left(\frac{-1}{r_a} \right) 1s_a + \int 1s_b \left(\frac{-1}{r_b} \right) 1s_b \\ &\quad + \int 1s_a \left(\frac{-1}{r_b} \right) 1s_a + \int 1s_b \left(\frac{-1}{r_a} \right) 1s_b \\ &\quad \left. + 4 \int 1s_a \left(\frac{-1}{r_b} \right) 1s_b \right], \end{aligned} \quad (4.21)$$

and we note that

$$\lim_{R \rightarrow \infty} \int 1s_a \left(\frac{-1}{r_b} \right) 1s_a = \frac{-1}{R}, \quad (4.22)$$

since a spherically symmetric orbital can be treated as point charge and we recover Coulomb's law. If we calculate these out, we find that with $\rho = \zeta R$,

$$\begin{aligned} S(R) &= e^{-\rho} \left[1 + \rho + \frac{1}{3}\rho^2 \right] \\ T_{ab}(R) &= \int 1s_a \left(-\frac{1}{2} \nabla^2 \right) 1s_b = -\frac{1}{2} \left[1 - \rho + \frac{1}{3}\rho^2 \right] e^{-\rho} \\ V_{aab} &= \int 1s_a \left(\frac{-1}{r_b} \right) 1s_a = \frac{-\zeta}{\rho} [1 + (1 + \rho)e^{-2\rho}] \\ V_{aba} &= \int 1s_a \left(\frac{-1}{r_b} \right) s_b = -\zeta(1 + \rho)e^{-\rho}. \end{aligned} \quad (4.23)$$

With these expressions, we can find $E_{var}^{(k=1)} + 1/R$ which would be the potential for the full molecular calculation. We could also calculate for $k = 2$. This will actually give fairly bad results for the dissociation energy, although fairly good results for the equilibrium radius. This is because the proton of the other nucleus will induce a polarization in the s orbitals and they will not be spherically symmetric. So since we are approximating the electronic wavefunction as a linear combination of spherically symmetric wavefunctions, we will not be able to get the answer right. We need to add a term to the wavefunction to account for it. The term needs to have the same symmetry as the initial wavefunctions, so we can use

$$2p_{0a} - 2p_{0b}, \quad (4.24)$$

and then perform the calculation.

4.2 Dihydrogen

Starting with the normal Hamiltonian, we would be tempted to write the wavefunction as

$$1\sigma_f^2 = |1\sigma_g \overline{1\sigma_g}| = \frac{1}{\sqrt{8(1+S)}} |(1s_a + 1s_b)(\overline{1s_a} + \overline{1s_b})|, \quad (4.25)$$

which we can write as

$$|1s_a \overline{1s_a}| + |1s_b \overline{1s_b}| + |1s_a \overline{1s_b}| + |1s_b \overline{1s_a}| = H^- H^+ + H^+ H^- + H : H + H : H, \quad (4.26)$$

two covalent terms and two ionic terms. This is not correct since we are saying we have half ionic and half covalent bonding. The electronic energy we calculate will not be right at the end points, and will be higher than the true energy (variation principle), however, it will be off by too much. The easiest way to fix this is to just get rid of the ionic terms. This is called Heitler-London theory. We can also allow for electron correlation and polarization of the orbitals. The last thing we will do is to allow for weighting of the ionic and covalent terms. The best way to do it is to write the wavefunction as

$$c_g |1\sigma_g \overline{1\sigma_g}| + c_u |1\sigma_u \overline{1\sigma_u}|, \quad (4.27)$$

which allows the molecule to dissociate correctly. In the single molecular orbital description, R_e is too small, ω_e is too large, and D_e is too small.

4.3 Homonuclear Molecules

The simplest homonuclear molecule is H_2^+ , which we have shown to be $|1\sigma_g|$. We have also discussed H_2 which is $1\sigma_g^2$. So we can define a bond order which is half the number of electrons in bonding orbitals minus half the number of electrons in antibonding orbitals. Notice that due to the lower denominator in the normalization factor for the anti-bonding orbital, it has a large effect than the bonding orbital. These cross terms raise the energy, the bonding cross terms lower the energy.

We can also construct higher order linear combination such as $2s_a \pm 2s_b$. This orbitals will be cylindrically symmetric, and we will call them $2\sigma_g$ and $2\sigma_u$ respectively. The classical example of this is Li_2 . We can write the electronic structure $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2$, which has a bond order of 1. The next homonuclear molecule is Be_2 , which is $1\sigma_g^2 \sigma_u^2 2\sigma_g^2 2\sigma_u^2$ and has a bond order of 0 and thus would not form.

Now we can consider the p orbitals. It is more complicated than the atomic case because we only have cylindrical symmetry instead of spherical symmetry. Thus, not all the p orbitals are symmetric. So we can take combinations like $2p_{za} \pm 2p_{zb}$ which are called $3\sigma_g$ and $3\sigma_u$ since they are symmetric. So here the bonding orbital is the $3\sigma_g$ orbital with the negative sign, opposite the case of the s combinations.

We can also make linear combinations of the x, y p orbitals. In order to get the spherical symmetry, we want linear combinations of the form

$$2p_{1a} + 2p_{1b}; 2p_{-1a} + 2p_{-1b}, \quad (4.28)$$

which are the π orbitals. So we define

$$1\pi_{ux} = \frac{1}{\sqrt{2(1+S)}}(2p_{xa} + 2p_{xb}) \quad (4.29)$$

$$1\pi_{uy} = \frac{1}{\sqrt{2(1+S)}}(2p_{ya} + 2p_{yb}), \quad (4.30)$$

which we take linear combinations as

$$1\pi_{u1} = \frac{1}{\sqrt{2}}(1\pi_{ux} + i1\pi_{uy}), \quad (4.31)$$

to get spherical orbitals out of the Cartesian ones. We can also get the antibonding orbitals (g orbitals in this case)

$$1\pi_{gx} = \frac{1}{\sqrt{2(1+S)}}(2p_{xa} - 2p_{xb}) \quad (4.32)$$

$$1\pi_{gy} = \frac{1}{\sqrt{2(1+S)}}(2p_{ya} - 2p_{yb}), \quad (4.33)$$

but we do not take combinations because they are not eigenfunctions of operators that commute with the Hamiltonian. So the $2p$ orbitals form three bonding and 3 antibonding orbitals.

One can characterize the total electronic state by specifying the overall cylindrical symmetry, the multiplicity $(2s+1)$, and the inversion symmetry. These are summarized in the term symbol usually written as

$$^{2s+1}\Lambda_{g/u}, \quad (4.34)$$

where Λ is the cylindrical symmetry, where we write

$$\Lambda = |M_L| = \left| \sum_{i=1}^N m_{l_i} \right|. \quad (4.35)$$

We write these as capital Greek letters Σ, Π, Δ , etc.

4.3.1 B_2

B_2 is a $^1\sigma_g^+$ and has configuration $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2$. Note that the plus means there is positive symmetry with regards to reflection in a plane containing the molecular axis. The bond order is 1, so it has a single bond. However, it is possible in theory to have a $1\pi_u^2$ instead of the $3\sigma_g^2$. So now we have to write the Slater determinant, we can write it one way as

$$|1\pi_{u1} 1\pi_{u-1}|, \quad (4.36)$$

where we have ignored the σ terms and π_{um} means the π orbitals with $m_l = m$. So we can note this state has $m_S = 1$ and $m_L = 0$ and after application of the S_- operator we have that

$$\frac{1}{\sqrt{2}} (|\pi_{u1} \bar{\pi}_{u-1}| + |\bar{\pi}_u \pi_{u-1}|), \quad (4.37)$$

where $m_L = m_S = 0$ and if we apply the lowering operator again, we get

$$|\bar{\pi}_{u1} \bar{\pi}_{u-1}|, \quad (4.38)$$

which is as $^3\Sigma_g$ state. To determine the parity, note that

$$\pi_{u1} \sim -e^{i\phi}; \pi_{u-1} \sim e^{-i\phi}, \quad (4.39)$$

and so

$$\hat{\sigma}_{xz} \pi_{u1} = -e^{-i\phi} = -\pi_{u-1} \quad (4.40)$$

and also that

$$\hat{\sigma}_{xz} \pi_{u-1} = -\pi_{u1}, \quad (4.41)$$

which means that when we operator on the determinant

$$\hat{\sigma}_{xz} |1\pi_{u1} 1\pi_{u-1}| = |1\pi_{u-1} 1\pi_{u1}| = -|1\pi_{u1} 1\pi_{u-1}| \quad (4.42)$$

which means the state is $^3\Sigma_g^-$. It turns out that this state has lower energy than the $^1\Sigma_g^+$. This makes sense since it is a triplet state and there is a tendency for electrons in triplet states to keep out of each others way as well as having a zero expectation value at the zero of the spherical coordinate system.

There are other ways we could assign the electrons such as $1\pi_{u1} 3\sigma_g$. This is an $m_L = 1$ state. We could also have $1\pi_{u-1} \sigma_g$ which would have $m_L = -1$. These two states will be degenerate since there is no determination of chirality in the Hamiltonian. It will be a Π_u state which could be either a singlet or a triplet depending on how we assign the electrons spins. These will not be degenerate. Note they will not have definite parity, for example

$$\hat{\sigma}_{xz} |1\pi_{u1} 3\sigma_g| = -|1\pi_{u-1} 3\sigma_g| \quad (4.43)$$

since rotation will not commute with orbitals that don't have spherical symmetry. However, if we take linear combinations of these two assignments, then we could get symmetry. So it doesn't make sense to label Π state \pm .

The only remaining option would be $|\pi_{u1} \bar{\pi}_{u-1}|$, which has $m_L = 2$ and so it will be a $^1\Delta_g$ state.

SD	M_L	M_S	State
$ 1\pi_{g\pm 1}1\bar{\pi}_{g\pm 1} $	2,-2	0	$^1\Delta_g$
$ 1\pi_{g1}1\pi_{g-1} $	0	-1,0,1	$^3\Sigma_g^-$
$ 1\pi_{u1}1\pi_{u-1} $	0	0	$^3\Sigma_g^-$
$\frac{1}{\sqrt{2}}(1\pi_1\bar{\pi}_- + \bar{\pi}_1\pi_{-1})$	0	0	$^1\Sigma_g^+$

Table 2: Possible Slater Determinant of O_2 .

4.3.2 O_2

Now we will talk about O_2 which will be more interesting than B_2 . So we can write this as

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 3\pi_{u1}^2 \pi_{u-1}^2 1\pi_g^2, \quad (4.44)$$

which has a bond order of 2, therefore a double bond. So we want to think about possibilities for $1\pi_g^2$. This is illustrated in table 2 So we have three states and the $^3\Sigma_g^-$ is the ground state. We can also write these in Cartesian orbitals $|\pi_x\pi_y|$, etc. When converting to Cartesian coordinates, we can take linear combinations of the possibilities to get completely imaginary or completely real Slater determinants which are orthogonal to each other. One of these is symmetric and one is not, which is why we do not specify the \pm in the way we would for a Σ state. We can evaluate the possibilities as

$$^3\Sigma_g^- = |\pi_x\pi_y|; \frac{1}{\sqrt{2}}[|\pi_x\bar{\pi}_y| - |\pi_y\bar{\pi}_x|]; |\bar{\pi}_x\bar{\pi}_y| \quad (4.45)$$

$$^1\Delta_g(x^2 - y^2) = \frac{1}{\sqrt{2}}[|\pi_x\bar{\pi}_x| - |\pi_y\bar{\pi}_y|] \quad (4.46)$$

$$^1\Delta_g(xy) = \frac{i}{\sqrt{2}}[|\pi_x\bar{\pi}_y| + |\pi_y\bar{\pi}_x|] \quad (4.47)$$

$$^1\Sigma_g^+ = \frac{1}{\sqrt{2}}[|\pi_x\bar{\pi}_x| + |\pi_y\bar{\pi}_y|] \quad (4.48)$$

If we try to calculate the energy, the only difference of these will be the electron repulsion terms. We talk about this in the same manner as we did the atomic case.

4.4 Heteronuclear Molecules

Now we examine molecules which have different atoms. We will first concentrate on molecules which are almost homonuclear.

4.4.1 CO^+

We can still write molecular orbitals, however, we do not have inversion as a molecular symmetry, but we still have rotation. So we no longer have g, u , so we have

$$1\sigma = 1s_C + 1s_O; 2s = 1s_C - 1s_O \quad (4.49)$$

instead of $1\sigma_g, 1\sigma_u$. So we can continue this with

$$3\sigma = \sin\theta 2s_C + \cos\theta 2s_O; 4\sigma = \cos\theta 2s_C - \sin\theta 2s_O. \quad (4.50)$$

We need the trigonometric functions since we cannot assume that the atomic orbitals are weighted the same since the nuclei are not heteronuclear. However, for close to homonuclear molecules, they are approximately weighted the same.

5 Spectroscopy

5.1 Electromagnetic Transitions

We start by defining an electric field in the \hat{z} direction

$$\vec{E} = E\hat{z} = \hat{z}E_0 \cos\left(2\pi\nu T - \frac{2\pi y}{\lambda}\right), \quad (5.1)$$

where ν is circular frequency, which is $\omega/2\pi$. This is a wave propagating in the y direction and oscillating the z direction. The magnetic field is oscillating in the x direction. This is given as

$$\vec{B} = B\hat{x} = \hat{y}B_0 \cos\left(2\pi\nu T - \frac{2\pi x}{\lambda}\right) \quad (5.2)$$

The magnitudes of these are given as

$$B_0 = \frac{E_0}{c}. \quad (5.3)$$

Since λ is generally much larger than atomic dimensions, we can treat y/λ as a constant over the dimensions of the atom. Let $T \rightarrow t + \gamma/\omega$ (changing zero of time), which allows us to rewrite \vec{E} as

$$\vec{E} = \hat{z}E_0 \cos(\omega t) \quad (5.4)$$

The Hamiltonian is given as

$$H = H_0(q, Q) + E(t)\hat{z} \quad (5.5)$$

We can treat this within perturbation theory by using states given by the time independent Schrodinger equation for the unperturbed Hamiltonian.

5.1.1 Time Dependant Perturbation Theory

We start with the time dependant Schrodinger equation which is given by

$$i\hbar \frac{\partial \Phi}{\partial t}(q, t) = H\Phi(q, t), \quad (5.6)$$

where q are the coordinates and t is time. If we write the Hamiltonian as

$$H = H_0(q) + V(q, t), \quad (5.7)$$

where we have separated H into time dependant and time independent parts, then we can write

$$\Phi_n(q, t) = e^{-i\omega_n^{(0)}t} \phi_n^{(0)}(q), \quad (5.8)$$

where $\omega_n^{(0)} = E_n/\hbar$, and

$$H_0\phi_n^{(0)}(q) = E_n^{(0)}\phi_n^{(0)}(q). \quad (5.9)$$

Now we can solve the full Schrodinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = (H_0 + V)\psi, \quad (5.10)$$

and by writing the full solution as

$$\Psi(q, t) = \sum_n c_n(t) \Phi_N^{(0)}(q, t) = \sum_n c_n(t) e^{-i\omega_n t} \phi_n^{(0)}(q). \quad (5.11)$$

Now, we substitute this back into the full equation, pre-multiply by $\phi_m^{(0)*}(q)$, and integrate over all coordinates except for time. Using the orthogonality of the wavefunctions, we obtain integrals of the form

$$\int e^{i\omega_m t} \phi_m^{(0)*}(q) V(q, t) \phi_n^{(0)}(q) e^{-i\omega_n t} dq = e^{i(\omega_m - \omega_n)t} \underbrace{\int \phi_m^{(0)*}(q) V(q, t) \phi_n^{(0)}(q) dq}_{V_{mn}(t)} \quad (5.12)$$

where we note the integral is really the matrix element of the perturbation. Now defining $\omega_m - \omega_n = \omega_{mn}$, then we have that

$$i\hbar \frac{\partial}{\partial t} c_m(t) = \sum_n e^{i\omega_{mn}t} V_{mn}(t) c_n(t), \quad (5.13)$$

which is a set of first order differential equations. We impose the boundary conditions

$$c_m(t=0) = \delta_{m,n}, \quad (5.14)$$

which says the system starts in some initial state $|n\rangle$. As time evolves, we must retain probability, so by noting that $c_m(t)$ is the probability amplitude of the system being in state $|m\rangle$, we note that

$$\sum_m |c_m(t)|^2 = \sum_m |c_m(0)|^2 = 1. \quad (5.15)$$

In the simplest approximation, we assume that $c_n(0) = 1$ and $|c_m(t)| \ll |c_n(t)|$, in other words $|V_{mn}|$ is small. So we can approximate these equations by

$$i\hbar \frac{\partial}{\partial t} c_m(t) = e^{i\omega_{mn}t} V_{mn}(t), \quad (5.16)$$

which says that

$$c_m(t) = -\frac{i}{\hbar} \int_{t_0}^t e^{i\omega_{mn}t} V_{mn}(t) dt \quad (5.17)$$

This is the first order perturbation theory.

5.1.2 Interaction of Light with Matter

We can define the energy flux as the energy per unit time per unit area, a vector quantity which is usually denoted \vec{S} and called the Poynting vector. It is directed along the propagation of the wave and so

$$\vec{S} \propto \vec{E} \times \vec{B}, \quad (5.18)$$

which implies that

$$\vec{S} \propto \frac{E_0^2}{c} \cos^2(\omega t) \hat{y}. \quad (5.19)$$

We can introduce the permeability μ_0 which will allow us to write

$$\frac{E_0^2}{\mu_0 c} \cos^2(\omega t) \hat{y}. \quad (5.20)$$

If we integrate over an entire cycle to get the average flux

$$\oint |S| = \frac{1}{2\mu_0 c} E_0^2, \quad (5.21)$$

which we can write in terms of the electric constant ϵ_0 defined as $\epsilon_0 \mu_0 = c^{-2}$, then we can write the average flux as

$$\oint |S| = \frac{c\epsilon_0}{2} E_0^2. \quad (5.22)$$

By considerations of kinetic theory, we know that the energy flux divided by the velocity will be the energy density. So

$$\rho = \frac{\epsilon_0}{2} E_0^2. \quad (5.23)$$

Now we note that

$$\vec{F} = Q\vec{E}, \quad (5.24)$$

where Q is a charge. Then, if we assume that $\vec{E} = E_0 \hat{z}$ (in practice we can usually transform coordinates such that this is true), then the potential can be found by integration as

$$V(x) = V_0 - QzE_0. \quad (5.25)$$

We will move the origin to let $V_0 = 0$ and so we have that

$$V(x) = E_z \sum_i q_i z_i, \quad (5.26)$$

which is a dipole operator. So in this case, we can write the potential as

$$V = -E_0 \cos(\omega t) \sum_i q_i z_i. \quad (5.27)$$

When evaluating the matrix elements, we need to integrate over both the electronic and nuclear wavefunctions, where the nuclear wavefunction will have both a vibrational and rotational component. So if we let

$$D_Z^{(m,n)}(\vec{R}) = \int \phi_{el}^{(m)*}(r; R) \hat{D}_z(r, R) \phi_{el}^{(n)}(r; R) dr \quad (5.28)$$

then for $m = n$, $D_Z^{(n,n)}(\vec{R})$ is the dipole moment of the molecule. If $m \neq n$, then this is the transition dipole moment. When we measure the dipole moment in a particular vibrational state, we actually measure

$$\langle v | D^{(n,n)}(R) | v \rangle, \quad (5.29)$$

which is an average of the dipole function over the vibrational wavefunction. For a transition from $v \rightarrow v'$, we get the average

$$\langle v | D^{(n,n)}(R) | v' \rangle. \quad (5.30)$$

To continue, note that there is no time dependence in evaluating this matrix element. So now we will switch notation from nm to if where $|i\rangle = |k''v''j''m''\rangle$ and $|f\rangle = |k'v'j'm'\rangle$. So if we define

$$M_{fi} = \langle k'v'j'm' | \hat{D}(r, R) | k''v''j''m'' \rangle, \quad (5.31)$$

as the transition dipole moment which is independent of time. So we can use perturbation theory to find

$$c_f(t) = -\frac{i}{\hbar} E_0 M_{fi} \int_{t_0=0}^t e^{i\omega_{fi}t'} \cos(\omega t') dt', \quad (5.32)$$

which we can integrate by using the exponential form the cos function which gives

$$c_f(t) = \frac{-iM_{fi}}{2\hbar} E_0 \left[\frac{e^{i(\omega_{fi}+\omega)t} - 1}{\omega_{fi} + \omega} + \frac{e^{i(\omega_{fi}-\omega)t} - 1}{\omega_{fi} - \omega} \right] \quad (5.33)$$

If we now assume that state $|f\rangle$ is higher than state $|i\rangle$, we can neglect the term with the addition in the denominator. Then if we take magnitude of this, we get that

$$|c_f(t)|^2 = \frac{E_0^2 |M_{fi}|^2}{\hbar^2} \frac{\sin^2((\omega_{fi} - \omega)t/2)}{(\omega_{fi} - \omega)^2} = \frac{E_0^2 |M_{fi}|^2}{4\pi^2 \hbar^2} \frac{\sin^2(\pi(\nu_{fi} - \nu)t)}{(\nu_{fi} - \nu)^2} \quad (5.34)$$

and if we replace $E_0^2 = 2\rho(\nu)/\epsilon$, we can write this as

$$|c_f(t)|^2 = \frac{\rho(\nu) |M_{fi}|^2}{\hbar^2 \epsilon_0 6\pi^2} \frac{\sin^2(\pi(\nu_{fi} - \nu)t)}{(\nu_{fi} - \nu)^2}, \quad (5.35)$$

where we have used the fact that only 1/3 of the photons are moving in one direction. This function is sharply peaked $\nu_{fi} - \nu = 0$ and falls sharply in both direction in ν space. At long time, this becomes even more peaked. This leads to the result that an atom only undergoes a transition when the frequencies exactly match. However, with short pulses, these transitions can occur over a range of frequencies. So we need to integrate our expression over all ν . If we perform this integral while making the assumption that $\rho(\nu) = \rho(\nu_{fi})$, we have the final result that

$$|c_{fi}(t)|^2 = \frac{t\rho(\nu_{fi})|M_{fi}|^2}{6\epsilon_0 \hbar^2} \quad (5.36)$$

This implies that

$$\frac{\partial |c_{fi}(t)|^2}{\partial t} = \frac{\rho(\nu_{fi})|M_{fi}|^2}{6\epsilon_0 \hbar^2} \quad (5.37)$$

which is the rate of absorption, a constant. So we now define the constant of proportionality as the Einstein B coefficient

$$B_{f \leftarrow i} = \frac{|M_{fi}|^2}{6\epsilon_0 \hbar^2}. \quad (5.38)$$

Since there is no sign dependence it means the rate of absorption and emission must be the same. The consequence of this is that unequal populations in two levels will equalize. Since they should not be the same at long time, they should instead be a Boltzmann distribution, so there must be a mechanism for which the populations can also change. This is referred to as spontaneous emission.

So now we note that B is a rate and has units of inverse time and the total rate at which energy is absorbed and emitted are given by $B_{fi}\rho(\nu)N_i$ and $B_{if}\rho(\nu)N_f$ respectively. However,

we must add in a term $A_{if}N_f$ which represents the spontaneous emission to keep the Boltzmann distribution satisfied. So this says that

$$AN_f + BN_F\rho = BN_i\rho, \quad (5.39)$$

which implies that

$$A = B\rho \frac{[N_i - N_f]}{N_f} = B\rho(e^{-(\epsilon_i - \epsilon_f)/k_B T} - 1), \quad (5.40)$$

where N is the total number and we have noted that $N_i = e^{-\epsilon_i/k_B T}$. Also we know that $\rho(\nu)$ is the energy density of the blackbody radiator which is given as

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/k_B T} - 1} \quad (5.41)$$

and if we note that $h\nu = \Delta E$, we can plug this in to get

$$A = \frac{8\pi h\nu^3}{c^3} \frac{|M_{fi}|^2}{6\epsilon_0 \hbar^2}, \quad (5.42)$$

where there are two important things to notice

1. Both A and B depend on $|M_{if}|^2$.
2. A has a ν^3 dependence.

5.1.3 Dipole Matrix Elements

We want to consider $|M_{fi}|^2$ since it is the only important non-trivial parameter in our expressions for lifetimes. So we have that if the state $|i\rangle$ depends on electronic state, vibrational state, and rotation state, then we can write

$$\psi = \phi_{el}^{(k)} \chi_v(R) Y_{jm}(\hat{R}), \quad (5.43)$$

and we want to calculate

$$\left\langle f \left| \sum_i q_i r_i \right| i \right\rangle, \quad (5.44)$$

where the sum is over electrons and nuclei. This integral is of the form

$$\int x_{vf}(R) Y_{j_fm_f}(\hat{R}) \phi_{el}^{(k_f)}(\vec{r}) D(\vec{r}, \vec{R}) \phi_{el}^{(k_i)} Y_{j_im_i}(\hat{R}) \chi_{v_i}(R) d\vec{r} d\vec{R} \quad (5.45)$$

So if we take the case where $k_f = k_i$, meaning the transition is within one electronic state, we can write the dipole operator as $D^{(k)}(\vec{R})$, which means it depends on the orientation of the molecule and the state. So we can write

$$D^{(k)}(\vec{R}) = \cos \Theta D^{(k)}(R), \quad (5.46)$$

where Θ is the angle between the molecular axis and the z axis. So this gives us

$$\int \chi_{v'}(R) D^{(k)}(R) \chi_{v''}(R) R^2 dR \int Y_{j'm'}(\hat{R}) \cos \Theta Y_{j''m''}(\hat{R}) \sin \Theta d\Theta d\Phi, \quad (5.47)$$

and we can consider each of these separately. We will note that

$$Y_{jm}(\Theta, \Phi) \propto P_{jm}(\cos \Theta) e^{im\Phi}, \quad (5.48)$$

and so we can consider the Θ and Φ dependencies separately.

For the Φ dependence, we have

$$\begin{aligned} \int Y_{j'm'}(\hat{R}) \cos \Theta Y_{j''m''}(\hat{R}) \sin \Theta d\Theta d\Phi &\sim \int d\Theta \int_0^{2\pi} e^{-m'\Phi} e^{im''\Phi} d\Phi, \\ &= \begin{cases} 0 & m' \neq m'' \\ 2\pi^2 & m' = m'' \end{cases} \end{aligned} \quad (5.49)$$

which says that $\Delta m = 0$ for a transition. Note this is only true for linearly polarized light. For circularly polarized light $\Delta m = \pm 1$. This is independent of the fact that $k_f = k_i$. Now we look at the j dependence

$$\int Y_{j'm'}(\hat{R}) \cos \Theta Y_{j''m''}(\hat{R}) \sin \Theta d\Theta d\Phi = \begin{cases} 0 & j' \neq j'' \pm 1 \\ x & j' = j'' \pm 1, \end{cases} \quad (5.50)$$

where x is some number. What's important to note is that $\Delta j = \pm 1$. We can calculate x for $j' = j'' + 1$ as

$$x = \sqrt{\frac{(j'' + m'' + 1)(j'' - m'' + 1)}{(2j'' + 1)(2j'' + 3)}}, \quad (5.51)$$

and it is important to note it depends on m . In the case that $j' = j'' - 1$, then we can write

$$x = \sqrt{\frac{(j'' + m'')(j'' - m'')}{(2j'' - 1)(2j'' + 1)}}. \quad (5.52)$$

If we now assume that $v'' = v'$, then we have a pure rotational transition. Note that if J increases by one, this is the R branch. If J decreases by one, this is the P branch. We are considering lower to upper (absorption) transitions. Also we know that since N_j is the Boltzmann distribution, transition of higher j will be less likely. The general intensity will be given for the R branch as

$$N_j \sum_{m''} \frac{(j'' + m'' + 1)(j'' - m'' + 1)}{(2j'' + 1)(2j'' + 3)} = N_j(j'' + 1). \quad (5.53)$$

Note that the overall absorption in the p branch is less since the stretched m states cannot transfer since $\Delta m = 0$.

5.2 Vibration-Rotation Energies of Diatomic Molecules

If we have two molecules A and B separated by R , then we can write the Hamiltonian as

$$H = -\frac{1}{2M_A} \nabla_A^2 - \frac{1}{2M_B} \nabla_B^2 + \frac{Z_A Z - B}{R} + V_{el}^{(k)}(R), \quad (5.54)$$

where we can write $\frac{Z_A Z - B}{R} + V_{el}^{(k)}(R) = V(r)$, where $V(r)$ is some potential, such as the Morse potential. We can now transform into coordinates $R_{cm}, \theta_{cm}, \phi_{cm}$, and $\vec{R} = R, \vec{\theta}, \vec{\phi}$, is the position of the coordinate axis in space, which gives

$$-\frac{1}{2M_A} \nabla_A^2 - \frac{1}{2M_B} \nabla_B^2 = -\frac{1}{2M} \nabla_{cm}^2 - \frac{1}{2\mu} \nabla_R^2, \quad (5.55)$$

where $M = M_A + M_B$ and $\mu = M_A M_B / (M_A + M_B)$. So we can write

$$E = E_{cm} + E_{int}, \quad (5.56)$$

the energy of the center of mass and the internal energy. The energies for E_{cm}

$$-\frac{1}{2M} \nabla_{cm}^2 \Psi(\vec{R}_{cm}) = E_{cm} \Psi(\vec{R}_{cm}), \quad (5.57)$$

which are just particle in a box energies. We can solve for E_{in} as

$$\left[-\frac{1}{2\mu} \nabla_R^2 + V(R) \right] \Psi(\vec{R}) = E_{in} \Psi(\vec{R}), \quad (5.58)$$

which means that

$$\Psi(\vec{R}) = Y_{j,m}(\vec{R}) R(R), \quad (5.59)$$

and projecting into spherical coordinates, we get that

$$\left[-\frac{1}{2\mu} \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + V(R) + \frac{j(j+1)}{2\mu R^2} \right] R(R) = E_{int} R(R). \quad (5.60)$$

We don't usually care about the E_{cm} in a spectroscopic experiment, and so we will focus on E_{int} . So we will make two approximations, the first is to approximate the potential as a harmonic oscillator and $R \rightarrow R_e$, which gives

$$V(r) + \frac{j(j+1)}{2\mu R^2} = -D_e + \frac{1}{2} k (R - R_e)^2 + \frac{1}{2\mu R_e^2} j(j+1), \quad (5.61)$$

note this is only valid around the minimum of the potential energy well and is essentially a power series expansion. So this gives that to lowest order

$$E_{int} = \hbar\omega \left(v + \frac{1}{2} \right) + \left[-D_e + \frac{\hbar^2}{2\mu R_e^2} j(j+1) \right], \quad (5.62)$$

and so we define $\hbar\omega = \omega_e$ and $\hbar^2/2\mu R_e^2 = B_e$. We can write ω as

$$\omega = \left(\frac{1}{\mu} \frac{\partial^2 V}{\partial R^2} \Big|_{R=R_e} \right)^{1/2}. \quad (5.63)$$

Typically ω_e on the order of hundreds to thousands of wavenumbers which is not very large and varies inversely to mass. B_e is on the order of tens of wavenumbers which quite small compared to ω_e .

5.2.1 Higher Order Terms

Now we can calculate this to higher orders by noting we have implicitly written

$$V(R) = V(R_e) + \frac{1}{2} k (R - R_e)^2 + \frac{1}{6} \frac{d^3 V}{dR^3} \Big|_{R=R_e} (R - R_e)^3 + \dots, \quad (5.64)$$

and also that

$$\frac{1}{R^2} = \frac{1}{(R_e + x)^2}, \quad (5.65)$$

where $x = R - R_e$ and is very small. So we can expand this in a Taylor series and get that

$$\frac{1}{R} \approx \frac{1}{R_e^2} \left(1 - 2\frac{x}{R_e} + 3\left(\frac{x}{R_e}\right)^2 + \dots \right), \quad (5.66)$$

and so we can consider a perturbing Hamiltonian

$$H' = \frac{1}{6} \frac{d^3 V}{dR^3} \Big|_{R=R_e} (R - R_e)^3 + \frac{1}{24} \frac{d^4 V}{dR^4} \Big|_{R=R_e} (R - R_e)^4 - \frac{2x}{2\mu R_e^3} j(j+1) + \frac{3x^2}{2\mu R_e^4} j(j+1), \quad (5.67)$$

and write corrections terms to E_{int} which we can evaluate using perturbation theory. For the first calculation, we need to calculate

$$E_v^{(1)} = \langle \phi_v^{(0)} | H' | \phi_v^{(0)} \rangle \propto \langle x^4 \rangle + j(j+1) \langle x^2 \rangle \quad (5.68)$$

since the wavefunctions are symmetric and only the even terms in H' will contribute. It turns out that $\langle x^4 \rangle$ increases in $(v + 1/2)^2$. One can calculate this using harmonic oscillator wavefunctions. Higher order perturbation theory will start to mix the odd terms into the energy. It turns out if the higher order terms are included

$$E_{int}(v, J) = -D_e + \omega_e \left(v + \frac{1}{2} \right) + B_e j(j+1) - \omega_e \chi_e \left(v + \frac{1}{2} \right)^2 - D_e [j(j+1)]^2 - \alpha_e \left(v + \frac{1}{2} \right) j(j+1) \quad (5.69)$$

where $\omega_e \chi_e$, the anharmonic parameter, is typically less than five percent of ω_e . D_e is not the same as the first D_e and is the centrifugal distortion parameter arising from a change R_e at higher j . α_e is the vibration rotation coupling cross term mixing the rotational and vibrational perturbations in second order, it has to do with the lack of symmetry of the true potential and is not in general small.

5.2.2 Transitions

We have already found the selection rules. We can easily use the expressions derived above to derive expressions for the energy transitions as

$$\Delta E = j'(j'+1)B_{v'} - j''(j''+1)B_{v''} + \omega_e \left(v' + \frac{1}{2} \right) - \omega_e \left(v'' + \frac{1}{2} \right) - \omega_e \chi_e \left(v' + \frac{1}{2} \right)^2 - \omega_e \chi_e \left(v'' + \frac{1}{2} \right)^2, \quad (5.70)$$

where we have written $B_v = B_e - \alpha_e(v + 1/2)$.

So we can define a band origin which is $|V'', J'' = 0\rangle \rightarrow |V', J' = 0\rangle$. This is not a transitions and will be between the P and R branch with P on the left and R on the right. If we have an electronic transition, the energy difference will be large (visible region of spectrum). We are really calculating

$$|\langle v' J' | D^{(k'', k')} (R) | v'' J'' \rangle|^2, \quad (5.71)$$

which is the dipole operator averaged over the electronic states where

$$D^{(k'', k')} = \int \phi_{el}^{(k')} (r; R)^* \hat{D}(R, r) \phi_{el}^{k''} (r; R) d\vec{r}. \quad (5.72)$$

There will be different transitions associated with the different electronic states. We know that the Dipole operator is the sum of one electron operators

$$D = \sum_i q_i \vec{r}_i, \quad (5.73)$$

and so the dipole operator will be zero unless the electronic states differ by one electron excitation. So in the case of N_2^+ , we can write the electronic states as

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^1 1\pi_u^4 \quad (5.74)$$

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^3 \quad (5.75)$$

and so if we consider this transition $1\pi_u \rightarrow 3\sigma_g$, then we need to consider

$$\int 1\pi_u q_i \vec{r}_i 3\sigma_g, \quad (5.76)$$

and we can impose a coordinate system. In this case if we take z to be the molecular axis, then the dipole moment operator will only have a dipole moment across x . Note since N_2^+ is homonuclear, it won't have any rotational transitions, since it doesn't have a dipole along the molecular axis.

We could consider $^2\Sigma_g^+$ and $^2\Sigma_u^+$. We will always have a dipole moment across the molecular axis. We need $g \rightarrow u$ or $u \rightarrow g$ for Σ states.

We can never have coupling between states whose spins are different.

When we have a perpendicular transition, we can also have a Q branch where $J'' \rightarrow j'$.

In general, we can write

$$E_{v''J''} = T_e'' + \frac{1}{2}\omega_e'' \left(v'' + \frac{1}{2} \right) + B_v'' J''(J'' + 1), \quad (5.77)$$

where $B_v = B_e - \alpha_e(v + 1/2)$, and so we can write

$$E_{v'J'} - E_{v''J''} = (T_e' - T_e'') + \omega_e' \left(v' + \frac{1}{2} \right) - \omega_e'' \left(v'' + \frac{1}{2} \right) + B_{v'} J'(J' + 1) - B_{v''} J''(J'' + 1), \quad (5.78)$$

and if we are considering the Q branch, we have

$$E_{v'J'} - E_{v''J''} = (T_e' - T_e'') + \omega_e' \left(v' + \frac{1}{2} \right) - \omega_e'' \left(v'' + \frac{1}{2} \right), \quad (5.79)$$

since $J' = J''$. However, the vibrational functions we worked out previously are not necessarily going to be orthogonal, and so the transition rules we worked out before do not apply. So we can consider a matrix of $\int \chi_{v'}^{(k')} D^{(k',k'')}(R) \chi_{v''}^{(k'')} dR$. In a single electronic state, there are diagonal elements, which is the dipole moment and each element away is induced by derivatives of the dipole moment operator with respect to R . However, if we are considering two different electronic states, the dipole moment will contribute on all elements, not just diagonal ones since the vibrational wavefunctions are not orthogonal. So we can approximate

$$\int \chi_{v'}^{(k')} D^{(k',k'')}(R) \chi_{v''}^{(k'')} dR = \int \chi_{v'}^{(k')} D(R) \chi_{v''}^{(k'')} dR, \quad (5.80)$$

where we have assumed $D(R)$ is a constant. The elements of this matrix are called Franck-Condon factors.

Note that ω_e is usually larger in the ground state since it is more tightly bound.

So now within each vibrational transitions, we have the rotational transitions as well. If we simple compute the R branch, we get that

$$\Delta E = (J'')^2(B_{v'} - B_{v''}) + J''(3B_{v'} - B_{v''}) + (2B_{v'} - B_{v''}), \quad (5.81)$$

and the P branch will be

$$\Delta E = (J'')^2(B_{v'} - B_{v''}) - J''(B_{v'} + B_{v''}) - (B_{v'} + B_{v''}). \quad (5.82)$$

So if we assume the most normal situation where $B'_v < B''_v$, but $3B'_v - B''_v > 0$. For the R branch the quadratic term will tend to move the lines to the left at high J and at some point, the transitions will lose the ordering, and experimentally this makes the lines hard to resolve as the lines clump. This is called a band head. For the P branch it will separate things out.

The Q branch will have

$$\Delta E = (B_{v'} - B_{v''})J''(J'' + 1), \quad (5.83)$$

and assuming that ΔB is small (usually the case), then there will be many closely spaced lines between the P and the R branch.