Dispersion Forces

by

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapters</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong></td>
<td>Introduction</td>
</tr>
<tr>
<td><strong>B</strong></td>
<td>Quantum Mechanics</td>
</tr>
<tr>
<td>B.i</td>
<td>The Hydrogenic Atom</td>
</tr>
<tr>
<td>B.ii</td>
<td>The Molecular Schrödinger Equation</td>
</tr>
<tr>
<td>B.iii</td>
<td>Variational theorem</td>
</tr>
<tr>
<td>B.iv</td>
<td>Perturbation theory</td>
</tr>
<tr>
<td><strong>C</strong></td>
<td>Dispersion forces</td>
</tr>
<tr>
<td>C.i</td>
<td>Classical Potential</td>
</tr>
<tr>
<td>C.ii</td>
<td>London model</td>
</tr>
<tr>
<td>C.ii.a</td>
<td>Damping function</td>
</tr>
<tr>
<td>C.iii</td>
<td>Spherical Atom Model</td>
</tr>
<tr>
<td>C.iv</td>
<td>Spherical atom model damping function</td>
</tr>
<tr>
<td><strong>D</strong></td>
<td>Computational Methods</td>
</tr>
<tr>
<td>D.i</td>
<td>Basis Sets</td>
</tr>
<tr>
<td>D.ii</td>
<td>Hartree Fock</td>
</tr>
<tr>
<td>D.iii</td>
<td>MPn’s - Many Body Perturbation Theory (MBPT)</td>
</tr>
<tr>
<td>D.iv</td>
<td>Couple cluster</td>
</tr>
<tr>
<td>D.v</td>
<td>Counterpoise correction</td>
</tr>
<tr>
<td>D.vi</td>
<td>Comment: The Density functional theory</td>
</tr>
<tr>
<td><strong>E</strong></td>
<td>Results I: Atomic Systems</td>
</tr>
<tr>
<td>E.i</td>
<td>Noble gas systems</td>
</tr>
<tr>
<td>E.i.a</td>
<td>He-He, Ne-Ne, Ar-Ar</td>
</tr>
<tr>
<td>E.i.b</td>
<td>He-Ne, He-Ar, Ne-Ar</td>
</tr>
<tr>
<td>Figures</td>
<td>60-80</td>
</tr>
</tbody>
</table>
E.ii “Organic” systems 80
  E.ii.a H-H, C-C 80-83
  E.ii.b H-C 83-85

Figures 85-89

F Results II: Molecular System H₂-NG 90
  F.i H-He, H-Ne, H-Ar 90-91
  F.ii H₂-He, H₂-Ne 92-98

Figures 99-104

G Results II: Molecular System F₂-NG 105
  G.i F-F 105-106
  G.ii F₂-He 106-109

Figures 110-113

H Conclusion 114-115
  H.i Comment 116

Figures 117-122

I Appendix 123-128

J References 129-133


DISPERSION FORCES

A Introduction

Quantum mechanics was first formulated in 1925 by Heisenberg, Born, and Jordan using matrices. Several months after, Schrödinger formulated quantum mechanics using differential equations and today, Schrödinger’s equation is the most widely known expression for quantum mechanics.

Currently, with increasing computational resources, quantum mechanics is now applied to many chemical systems. *Ab initio* methods on gas phases are elaborately developed and are capable of calculating electronic structures and properties of small molecules. These calculations provide useful theoretical insights to experimentally unobtainable chemical properties.

In this thesis, highly sophisticated computational methods will be used to study and develop a new mathematical model to describe long range interactions between nonpolar atoms and molecules.
B Quantum Mechanics

The Schrödinger equation, given below, is the quantum mechanical version of the Newton’s force law in classical mechanics:

\[-\frac{i\hbar}{\partial t} \frac{\partial \Psi(x_1,x_2,\ldots;t)}{\partial t} = -\frac{\hbar^2}{2m} \sum_i \frac{\partial^2 \Psi(x_1,x_2,\ldots;t)}{\partial x_i^2} + V(x_1,x_2,\ldots)\Psi(x_1,x_2,\ldots;t)\]  

(b-1)

where the wavefunction $\psi$ describes the motion of the particles and the potential energy $V$ describes the nontranslational energetics of the system. If the potential is time independent, the Schrödinger equation can be converted into a time independent equation:

\[-\frac{\hbar^2}{2m} \sum_i \frac{\partial \psi(x_1,x_2,\ldots)}{\partial x_i} + V(x_1,x_2,\ldots)\psi(x_1,x_2,\ldots) = E\psi(x_1,x_2,\ldots).\]  

(b-2)

Equation (b-2) is an eigenfunction-eigenvalue problem where the eigenvalue is the energy of the system and the eigenfunction is the wavefunction. The boundary conditions for the wavefunction will lead to a quantized energy spectrum.

The Schrödinger equation can be written using operator mechanics such that

\[\hat{H}\psi = E\psi,\]  

(b-3)

where $\hat{H}$ is the Hamiltonian operator that consists of the kinetic and the potential energy operators. If the Hamiltonian can be written as a sum in terms of independent coordinates,

\[\hat{H}(x_1,x_2,\ldots) = \sum_i \hat{H}_i(x_i),\]  

(b-4)

the wavefunction can be written as a product:

\[\psi(x_1,x_2,\ldots) = \Pi_i \psi_i(x_i)\]  

(b-5)

and the energy can be written as sum:
\[
E = \sum_i E_i \tag{b-6}
\]

where

\[
\hat{H}_i \psi_i = E_i \psi_i \tag{b-7}
\]

The eigenfunctions of the Schrödinger equation form a complete set in the Hilbert space. That is:

\[
\psi(\tau) = \sum_{n=1}^{\infty} c_n \psi_n(\tau), \tag{b-8}
\]

such that any function satisfying the same boundary conditions can be expressed as a linear combination of \( \psi_n \). The wavefunction has a probabilistic interpretation in that \( |\psi(\tau)|^2 \) is the probability density of finding a particle at \( \tau \). The wavefunction is then required to be square-integrable:

\[
\int |\psi(\tau)|^2 \, d\tau = 1 \tag{b-9}
\]

so that the particle is quantized – the total probability that the particle is somewhere equals one.

The expectation value or the average value of any observable measured with the operator \( \hat{A} \) can be expressed as

\[
< \hat{A} > = \int \psi^*(\tau) \hat{A} \psi(\tau) \, d\tau. \tag{b-10}
\]

In Dirac’s bra-ket notation, where the bra vector, \( < \psi(\tau) | \), is the adjoint of the ket vector, \( |\psi(\tau) > \), the expectation value can be written as

\[
< \hat{A} > = < \psi(\tau) | \hat{A} | \psi(\tau) > \tag{b-11}
\]

where the wavefunction satisfies the criteria that

\[
< \psi | \psi > = 1. \tag{b-12}
\]
B.i  The Hydrogenic Atom

For a hydrogenic atom consisting of a nucleus with charge Ze and an electron with charge -e, the electronic Schrödinger equation in spherical coordinates can be written as

\[ \frac{-\hbar^2}{2\mu} \nabla^2 \psi(r, \theta, \phi) - \frac{Ze^2}{4\pi\varepsilon_0 r^2} \psi(r, \theta, \phi) = E \psi(r, \theta, \phi) \]  

(b.i-1)

where the Laplacian operator is

\[ \nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}. \]  

(b.i-2)

It can be shown that the Hamiltonian can be separated into terms that only depend on r and into terms that only depend on the angles (as shown in equations (b-4) to (b-6)). Solving the angular component will show that the eigenfunctions are the spherical harmonics that can be written as:

\[ Y_l^m(\theta, \phi) = \sqrt\frac{(2l+1)(l+|m|)!}{4\pi(l+|m|)!} \exp(im\phi)P_l^m(\cos \theta). \]  

(b.i-3)

The azimuthal quantum number \( l \) that describes the angular momentum and the magnetic quantum number \( m \) that describes the orientation of the angular momentum arise from quantized angular states. The radial component of the wavefunction is described by Laguerre polynomials:

\[ L_q(x) = e^x \left( \frac{d}{dx} \right)^q e^{-x} x^q. \]  

(b.i-4)

The hydrogenic wavefunction then can be expressed as
\[
\psi_{nlm} = R_n(r)Y_l^m(\theta, \varphi) = \left( \frac{2}{\text{na}} \right)^\frac{3}{2} \frac{(n-l+1)!}{2n(n+1)!} e^{-\frac{2r}{\text{na}}} \left[ L_{n-l-1}^l \left( \frac{2r}{\text{na}} \right) \right] Y_l^m(\theta, \varphi), \quad \text{(b.i-5)}
\]

where linear combination of the degenerate complex spherical harmonics in conjunction with the discrete energy level will give the 1s, 2s, 2p, 3s, … orbitals generally employed by chemists.

**B.ii The Molecular Schrödinger Equation**

For systems with more than one electron, the Schrödinger equation becomes:

\[
-\frac{\hbar^2}{2} \sum_{a} \frac{1}{m_a} \nabla_a^2 - \frac{\hbar^2}{2m_i} \sum_{i} \nabla_i^2 + \frac{1}{4\pi\varepsilon_0} \sum_{\text{electrons}} \sum_{a} \frac{Z_a e^2}{r_{ia}} + \sum_{\text{electrons}} \sum_{j} \frac{e^2}{r_{ij}} + \sum_{\text{nuclei}} \sum_{a, b} \frac{Z_a Z_b e^2}{r_{ab}} = 0, \quad \text{(b.ii-2)}
\]

The Born-Oppenheimer approximation\(^5\) can be made where the nuclear motions can be separated as in equations (b-4) to (b-6) (since the masses of the nuclei are much greater than that of electrons). The Schrödinger equation can be rewritten in terms of electronic and nuclear Hamiltonians:

\[
\hat{H}\psi = (\hat{H}_e + \hat{H}_N)\psi_e\psi_N = \psi_e \hat{H}_e \psi_e + \psi_N \hat{H}_N \psi_N, \quad \text{(b.ii-3)}
\]

where

\[
\hat{H}_e = -\frac{\hbar^2}{2m_e} \sum_{i} \nabla_i^2 - \sum_{a} \sum_{i} \frac{Z_a e^2}{r_{ia}} + \sum_{j} \sum_{i,j} \frac{e^2}{r_{ij}}. \quad \text{(b.ii-4)}
\]

Although the electronic portion of the Hamiltonian usually contains the information about chemical properties of the system, because of the interelectronic repulsion term, the Schrödinger equation is analytically unsolvable.
**B.iii Variational theorem**

The variational theorem states that any function that is not the true eigenfunction of the system will give an upperbound to the ground state energy:

\[
\int \phi^* \hat{H} \phi \, d\tau \geq E_1. \tag{b.iii-1}
\]

Therefore, using a trial wavefunction, the estimate of the energy and the wavefunction can be iteratively solved (using the variational theorem) until the energy and the wavefunction are relatively converged to a specified criteria\(^6\).

**B.iv Perturbation theory**

The perturbation theory is an approximate method that attempts to solve the Schrödinger equation based on a similar system where the eigenfunctions and the eigenvalues are known. The perturbation theory breaks up the Hamiltonian into

\[
\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)} \tag{b.iv-2}
\]

where \(\hat{H}^{(0)}\) represents the unperturbed system that can be solved exactly and \(\hat{H}^{(1)}\) is the perturbation that makes the system unsolvable. The parameter \(\lambda\) is the perturbation parameters for “bookkeeping;” when \(\lambda\) is zero, the system is unperturbed and when \(\lambda\) is one, the system is fully perturbed. The wavefunction and the energy can also be expressed in terms of \(\lambda\) as a power series:

\[
\psi = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \ldots \tag{b.iv-3}
\]

\[
E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots \tag{b.iv-4}
\]

Altogether, \(\hat{H}\psi = E\psi\) can be written as
\begin{align*}
(\hat{H}^{(0)} + \lambda \hat{H}^{(1)} + \lambda^2 \hat{H}^{(2)} + \ldots)(\psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \ldots) \\
= (E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots)(\psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \ldots)
\end{align*}

Taking all the like powers of \( \lambda \) will give each order of perturbation where the first order perturbation energy calculates to be:

\[ E_n^{(1)} = \left\langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(0)} \right\rangle \]  

with the first order wavefunction:

\[ \psi_n^{(1)} = \sum_{m=n} \left( \frac{\left\langle \psi_m^{(0)} | H^{(1)} | \psi_n^{(0)} \right\rangle}{(E_n^{(0)} - E_m^{(0)})} \right) \psi_m^{(0)}. \]  

The second, third, and fourth order energy can be expressed as

\[ E_n^{(2)} = \sum_{m=n} \left( \frac{\left\langle \psi_m^{(0)} | \hat{H}^{(1)} | \psi_n^{(0)} \right\rangle^2}{(E_n^{(0)} - E_m^{(0)})} \right) \]  

\[ E_n^{(3)} = \sum_{j=n} \sum_{m=n} \frac{\left\langle \psi_n^{(0)} | \hat{H}^{(1)} - E_n^{(1)} | \psi_m^{(0)} \right\rangle \left\langle \psi_m^{(0)} | \hat{H}^{(1)} - E_n^{(1)} | \psi_j^{(0)} \right\rangle \left\langle \psi_j^{(0)} | H^{(1)} | \psi_n^{(0)} \right\rangle}{(E_j^{(0)} - E_m^{(0)}) (E_n^{(0)} - E_j^{(0)})} \]  

\[ E_n^{(4)} = \sum_{i=n} \sum_{j=n} \sum_{k=n} \frac{\left\langle n | H^{(1)} | i \right\rangle \left\langle i | H^{(1)} - E_n^{(1)} | j \right\rangle \left\langle j | H^{(1)} - E_n^{(1)} | k \right\rangle \left\langle k | H^{(1)} | n \right\rangle}{(E_i^{(0)} - E_j^{(0)}) (E_j^{(0)} - E_k^{(0)}) (E_k^{(0)} - E_i^{(0)})} - E_k^{(2)} \left\langle \psi_k^{(1)} | \psi_k^{(1)} \right\rangle. \]  

As more perturbation terms are included in (b.iv-3) and (b.iv-4), the approximation will be closer to the exact answer.
C Dispersion forces

Dispersion forces are long range interactions between instantaneous and induced multipole moments that result from electron correlation between interacting monomers (see Section D.i-ii.). At long ranges, dispersion energy will dominate and as the monomers approach each other, the motions of the electrons will become more constrained and repulsion will dominate over dispersion (and other correlation effects). The balance between these two forces will influence the equilibrium geometry and the energy.

C.i Classical Potential

• Point Dipole

The simplest van der waals interaction to consider is that between dipole 1 described a pair of oppositely charged particles $e_a$ and $-e_a$; dipole 2 likewise is described by a pair of oppositely charged particle $e_b$ and $-e_b$. The configuration is shown in Diagram (c.i-1).

The total potential energy can be expressed as:

$$ V = \frac{e_a e_b}{R} + \frac{e_a e_b}{r_{12}} - \frac{e_b e_a}{r_{1b}} - \frac{e_b e_a}{r_{2a}} + \left[ \frac{e_a^2}{r_{1a}} - \frac{e_b^2}{r_{2b}} \right]. $$

(c.i-1)
where there will be attractive coulomb interactions between the oppositely charged points and repulsive interactions between the like-charged points.

The terms outside the bracket in equation (c.i-1) represents the total external field on both the systems. This represents the intermolecular potential energy:

$$V = \frac{e_x e_b}{R} + \frac{e_x e_b}{r_{1b}} - \frac{e_x e_b}{r_{2a}}.$$  (c.i-2)

This potential can be transformed into the Cartesian coordinates of dipole 1 \(\{x_1, y_1, z_1\}\) and dipole 2 \(\{x_2, y_2, z_2\}\) such that:

$$r_{12}^{-1} = [(R + z_2 + z_1)^2 + (x_1 - x_2)^2 + (y_1 - y_2)^2]^{1/2},$$  (c.i-3a)

$$r_{1b}^{-1} = [(R - z_1)^2 + x_1^2 + y_1^2]^{1/2},$$  (c.i-3b)

and

$$r_{2a}^{-1} = [(R + z_2)^2 + x_2^2 + y_2^2]^{1/2}.$$  (c.i-3c)

Using the Taylor series given below:

$$\left(1 + x\right)^{-1/2} = 1 - \frac{1}{2} x^2 + \frac{1}{8} x^3 + ..., \quad (c.i-4)$$

if the first term in (c.i-3a) is factored out to give (c.i-5a),

$$r_{12}^{-1} = \frac{1}{\sqrt{(R^2 + 2Rz_1 + 2z_2 z_1 + z_1^2 + z_2^2 + (x_1 - x_2)^2 + (y_1 - y_2)^2)}},$$  (c.i-5a)

the internuclear distance can be factored out to give (c.i-5b). Expandind (c.i-5a) will then give:

$$r_{12}^{-1} = \frac{1}{R} \left[ 1 + \frac{(2Rz_1 + 2Rz_2 + 2z_1 z_2 + z_1^2 + z_2^2)}{R^2} + \frac{(x_1 - x_2)^2}{R^2} + \frac{(y_1 - y_2)^2}{R^2} \right]^{-1/2}$$  (c.i-5b)

$$= \frac{1}{R} \left[ 1 - \frac{z_2 - z_1}{R} \frac{1}{2} \frac{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}{R^2} + \frac{3}{2} \frac{(z_1 - z_2)^2}{R^2} + ... \right]$$  (c.i-5c)

Similarly for (c.i-3b) and (c.i-3c), \(r_{1b}\) and \(r_{2a}\) can be written as
Substituting (c.i-5c), (c.i-6b), and (c.i-7b) into equation (c.i-2) will give the final form of the potential energy to be

\[ V = e_x e_b \frac{x_1 x_2 + y_1 y_2 - 2z_1 z_2}{R^3} + ... \]  

(c.i-8a)

that can also be expressed as:

\[ V = \frac{p_{x_1} p_{x_2} + p_{y_1} p_{y_2} - 2p_{z_1} p_{z_2}}{R^3} + ... \]  

(c.i-8b)

where \( e_x \), \( e_y \), and \( e_z \) are the directional components of the dipole moment \( \mathbf{p} \).

Equation (c.i-8b) shows that the interaction energy of the two dipoles depends on the net dipole moment of the system.

- **Point charge distribution potential**

Now a cluster of charged particles representing an atom is considered. If \( R \) is the distance between the origin of the cluster and a reference point, as shown in Diagram (c.i-2), the potential \( \phi \) is given by (c.i-9):
\[ \phi(\vec{R}) = \sum_{i} \frac{e_i}{|\vec{R} - \vec{r}_i|} \]  

(c.i-9)

\[ (c.i-10) \]

where \( e_i \) is the charge of point \( i \) at distance \( r_i \) from the origin:

For \( \vec{R} \) represented by Cartesian coordinates \( \{X, Y, Z\} \) and \( r_i \) by \( \{x_i, y_i, z_i\} \),

\[ |\vec{R} - \vec{r}_i|^{1/2} \]

can be written as:

\[ [(X-x_i)^2 + (Y-y_i)^2 + (Z-z_i)^2]^{1/2}. \]

If (c.i-10) is expanded to give

\[ [(X^2 + Y^2 + Z^2) - 2(Xx_i + Yy_i + Zz_i) + (x_i^2 + y_i^2 + z_i^2)]^{1/2} \]

(c.i-11a)

\[ \frac{1}{R} \left[ 1 - \frac{2(Xx_i + Yy_i + Zz_i) + (x_i^2 + y_i^2 + z_i^2)}{R^2} \right]^{1/2}, \]

(c.i-11b)

the Taylor expansion for (c.i-11b) gives

\[ \phi(\vec{R}) = \sum_{R} e_i + \frac{1}{R} \left[ \sum_{R} \frac{X}{R} e_i x_i + \sum_{R} \frac{Y}{R} e_i y_i + \sum_{R} \frac{Z}{R} e_i z_i \right] + ... \]

(c.i-12a)

Note that equation (c.i-12a) can be written as

\[ \phi(\vec{R}) = \frac{q}{R} + \frac{\vec{R} \cdot \sum_{R} e_i \vec{r}_i}{R^3}. \]

(c.i-12b)
This shows that the potential depends on the total net charge $q$ and the net dipole moment of the cluster.

- **Two charge distribution interaction**

  The interaction energy between two clusters of charges each representing a monomer will be calculated using the result given in equation (c.i-12a). The potential energy derived in this section will be used to derive the London model for dispersion forces.

  The potential energy representing the interaction between cluster 1 and cluster 2 where the two origins are separated by a distance $R$ is given by (c.i-13):

  \[
  V(R) = \sum e_i \phi(R + \vec{r}_i) \tag{c.i-13}
  \]

  Note that (c.i-13) can be rewritten as:

  \[
  V(R) = \sum_{i,j} \frac{e_i e_j}{|R - \vec{r}_j + \vec{r}_i|} \tag{c.i-14}
  \]

  where distance $r_j$ is the displacement of charge $e_j$ in the second cluster to the origin of the first cluster. This configuration is shown in Diagram (c.i-3).

![Diagram](c.i-3)

The Taylor expansion is used again by first writing (c.i-14) as:
| \((\mathbf{R} - \mathbf{r}_i) + \mathbf{r}_j\)|\(^{-1}\) = \([((X-x_i+x_j)^2 + (Y-y_i+y_j)^2 + (Z-z_i+z_j)^2] \) (c.i-15)

\[
|\mathbf{R} - \mathbf{r}_i|^{-1} = |\mathbf{R} - \mathbf{r}_i|^{-1/2} \left(1 + \frac{2\mathbf{R} \cdot \mathbf{r}_i}{|\mathbf{R} - \mathbf{r}_i|} \right)^{-1/2} \) (c.i-16)

Vector \(\mathbf{r}_j\) is described the coordinates \(\{x_j, y_j, z_j\}\). Expanding the potential will give:

\[
V(\mathbf{R}) = \sum_i e_i e_j \left(1 - \frac{\mathbf{R} \cdot \mathbf{r}_i}{|\mathbf{R} - \mathbf{r}_i|} - \frac{\mathbf{r}_i \cdot \mathbf{r}_j}{|\mathbf{R} - \mathbf{r}_i|} + \ldots \right). \) (c.i-17)

Note that the term that multiplies the bracket in equation (c.i-17) is the potential of cluster 1.

Expanding \(|\mathbf{R} - \mathbf{r}_i|^{-1}\) in equation (c.i-17) gives:

\[
V(\mathbf{R}) = \frac{1}{R^3} \sum_i e_i e_j \left[\mathbf{r}_i \cdot \mathbf{r}_j - \frac{(\mathbf{r}_i \cdot \mathbf{R})(\mathbf{r}_j \cdot \mathbf{R})}{R^2} + \ldots \right]. \) (c.i-18)

Converting (c.i-18) into Cartesian coordinates will give the final expression of the potential to be

\[
V(\mathbf{R}) = \frac{1}{R^3} \sum_i e_i e_j (x_i x_j + y_i y_j - 2z_i z_j) + \ldots \) (c.i-19a)

\[
= \frac{1}{R^3} \sum_{i,j} p_{ai} p_{aj} + p_{ai} p_{aj} - 2p_{ai} p_{aj} + \ldots \) (c.1-19b)

Equation (c.i-19a) is the classical interpretation of the interaction between two monomers and shows that the interaction depends on the net dipole moment of each monomer.

**C.ii London model**

- **Derivation**

From expression (c.i-19a-b), if either one of the monomer is nonpolar, the
interaction energy of the system is zero. London however showed that nonpolar species are capable of having weak electrostatic interactions.

If equation (c.i-19a) is rewritten so that \( e_i = e_j = e \) where \( e \) is the charge of the electron and \( X = \sum x_i \), \( Y = \sum y_i \), \( Z = \sum z_i \), the first order perturbation energy is expressed as

\[
E^{(1)} = \langle \psi_0 \left| \frac{e^2}{R^3} \left( X X + Y Y - 2 Z Z \right) \right| \psi_0 \rangle. \tag{c.ii-1}
\]

If the negative charges on each cluster is spherically distributed, the first order energy is zero since \( X_a = Y_a = Z_a \) or/and \( X_b = Y_b = Z_b \). When equation (c.ii-1) is rewritten as:

\[
E^{(1)} = \langle \psi_0 \left| \frac{p_i^1 p_i^2 + p_j^1 p_j^2 - 2 p_i^1 p_j^2}{R^3} \right| \psi_0 \rangle, \tag{c.ii-2}
\]

atoms and molecules with nonpermanent dipole moments (ie: nonpolar molecules), will have zero first order energy.

Now calculating the second order energy, using the shorthand notation:

\[
X_{mn} = \langle \psi_n^{(0)} \left| \frac{eX}{R^3} \right| \psi_0 \rangle, \text{...} \tag{c.ii-4}
\]

the ground state second order energy is expressed as:

\[
E^{(2)} = \frac{e^4}{R^6} \sum_{m,n=\pm} \frac{|X_{mn}^1 X_{mn}^2 + Y_{mn}^1 Y_{mn}^2 - 2 Z_{mn}^1 Z_{mn}^2|^2}{(E_1^m - E_1^n) + (E_2^m - E_2^n)}. \tag{c.ii-5}
\]

Note that the \( R^{-6} \) dependence arises from the fact that the matrix element is squared; the integrals for each matrix element can also be decoupled since A and B are expressed in terms of independent coordinates. Equation (c.ii-5) can be simplified if the second order energy is averaged over all orientation of both clusters 1 and 2. This would make the cross terms cancel when the numerator is squared to give:
\[
\left\langle E_{\epsilon_{\alpha}}^{(ii)} \right\rangle = \frac{e^4}{R^4} \sum_{m,n \neq 0} \frac{|X_{mn}^1|^2 |X_{mn}^2|^2 + |Y_{mn}^1|^2 |Y_{mn}^2|^2 + 4|Z_{mn}^1|^2 |Z_{mn}^2|^2}{(E_0 - E_{\epsilon_{\alpha}}^1) + (E_0 - E_{\epsilon_{\alpha}}^2)}. 
\]

(c.ii-6)

If the discrete charge distributions for both A and B are spherically symmetric then:

\[X^2 = Y^2 = Z^2 = \frac{1}{2} R^2\]  

(c.ii-7)

and (c.ii-6) can be written as:

\[
E = \frac{e^4}{R^4} \sum_{m,n \neq 0} \frac{\frac{1}{3} |R_{mn}^1|^2 |R_{mn}^2|^2 + \frac{1}{7} |R_{mn}^1|^2 |R_{mn}^3|^2 + 4(\frac{1}{5} |R_{mn}^1|^2 |R_{mn}^2|^2)}{(E_0 - E_{\epsilon_{\alpha}}^1) + (E_0 - E_{\epsilon_{\alpha}}^2)}. 
\]

(c.ii-8a)

\[
= \frac{2e^4}{3R^4} \sum_{m,n \neq 0} \frac{|R_{mn}^1|^2 |R_{mn}^2|^2}{(E_0 - E_{\epsilon_{\alpha}}^1) + (E_0 - E_{\epsilon_{\alpha}}^2)}. 
\]

(c.ii-8b)

The summation in (c.ii-8b) can be approximated if the quantum mechanical expression for polarizability is used:

\[
\alpha = \frac{2e^2}{3 \hbar} \sum \frac{\nu_{j0} |R_{j0}|^2}{\nu_{j0}^2 - \nu^2}. 
\]

(c.ii-9)

where \(\nu_{j0}\) is the frequency (\(\Delta E/\hbar\)) corresponding to the transition from the unperturbed state to state \(j\) when an electric field with frequency \(\nu\) is applied. In a static field (\(\nu = 0\)), the polarizability becomes:

\[
\alpha(0) = \frac{2e^2}{3 \hbar} \sum \frac{\nu_{j0} |R_{j0}|^2}{\nu_{j0}^2} = \frac{2e^2}{3} \sum \frac{|R_{j0}|^2}{E_j - E_0}. 
\]

(c.ii-10)

The energy difference in denominator can be approximated as the ionization energy, \(I\), and the polarizability can be written as:

\[
\alpha(0) = \frac{2e^2}{3 \hbar} \frac{1}{I} \sum |R_{j0}|^2. 
\]

(c.ii-11)

Before this definition is substituted into (c.ii-8b), note that the same approximation for the ionization energy can be made in (c.ii-8b) where the energy difference in the
denominator can be expressed as \( I = E_0 - E_m \) to give:

\[
E \approx -\frac{2e^i}{3R^6} \frac{1}{I_1 + I_2} \sum_i |R_{\infty}^i|^2 |R_{\infty}^i|^2.
\]  
\[\text{(c.ii-12)}\]

Substituting (c.ii-11) into (c.ii-12) gives:

\[
E \approx -\frac{3}{2} \frac{1}{I_1 + I_2} \frac{\alpha(0)\alpha(0)}{R^6}.
\]  
\[\text{(c.ii-13)}\]

that can be expressed as:

\[
E \approx -\frac{C_s}{R^6},
\]  
\[\text{(c.ii-14)}\]

where \( C_s = \frac{3}{2} \frac{1}{I_1 + I_2} \alpha \cdot \alpha \) describes the interaction between two nonpermanent dipoles characterized by their polarizability. Equation (c.ii-14) shows that contrary to classical treatment, quantum mechanics describes dispersion forces with \( R^{-6} \) dependence.

Note that when the potential energy was initially expanded, all the higher order terms other than the first term were expressed as “…”. These higher order terms were not written out for simplicity. However, they are critical to describe the system accurately. The infinite binomial expansion would give infinite number of terms to describe dispersion where the second term has \( R^{-4} \) dependence that describes the dipole-quadrupole interaction, the third term has \( R^{-5} \) dependence describes the quadrupole-quadrupole interaction, etc.. Including these infinite numbers of terms in the perturbation treatment would give rise to terms such that the total potential energy \( E \) can be expressed as:

\[
E = -\frac{C_s}{R^6} - \frac{C_4}{R^4} - \frac{C_{10}}{R^{10}} + \ldots = -\sum_{n=3}^{\infty} \frac{C_{2n}}{R^{2n}}.
\]  
\[\text{(c.ii-15)}\]
Equation (c.ii-15) is the London model where $C_{2n}$ are called dispersion coefficients.

- **Comments**

  Because large $R$ was assumed in the Taylor series expansion, the multipole expansion is divergent for short distances and is only valid for $R \geq \langle r \rangle$ where the series converges.

**C.iii  Damping function**

When the two monomer electron densities are not overlapping, each monomer electron density is polarized by the nearby atom such that the two atoms are pulled towards each other by dispersion interaction. However, as shown in Diagram (c.iii-1), when the atomic spheres begin to overlap, the overlapping densities are polarized in the opposite directions such that these overlapping regions produce forces that pull the two spheres apart. The net dispersion interaction in this region is then zero. When the two densities are completely overlapping and the nuclei fused, the total dispersion interaction is zero and the intramolecular/atomic energy makes up the energy of the system. The London model fails to describe this behavior and damping functions are introduced to take into account overlap effects\textsuperscript{13}.

The damping function that will be described here will be the Tang and Toennies damping function\textsuperscript{14} where the function was specifically developed to correct
the mathematically diverging behavior of the London model as more terms are included in the multipole expansion and to correct the influence of electron overlap. The corrected multipole expansion is written as:

\[ V_{\text{disp}} = -\sum_{n=3}^{\infty} f_{2n} \frac{C_{2n}}{R^{2n}} \]  

(c.iii-1)

where the damping function \( f_{2n} \) is

\[ f_{2n}(R) = 1 - \sum_{k=0}^{2n} \frac{(bR)^k}{k!} \exp(-bR). \]  

(c.iii-2)

Equation (c.iii-2) has the behavior \( f_{2n}(R \to \infty) \to 1 \) and \( f_{2n}(R \to 0) \to 0 \) for each multipole term. As the multipole term gets larger, the \( f_{2n} \) will be a smaller fraction of one to cancel the negative diverging behavior.

C.iv Spherical Atom model

The derivation of the London model was based on discrete spherical distributions of charges. In reality, this description of atoms or molecules is unrealistic since atoms in quantum mechanics are described as continuous distributions of charges. A new mathematical model for dispersion forces will be reformulated by applying the London model to a continuous distribution of charges on a spherical shell.

- Point-Sphere Model

In order to describe interaction between two spherical shells, the potential between a point charge and a spherical shell will be derived first. Truncating the London model to one term, the potential energy is expressed as:
\[ V(R) = -\frac{C_6}{R^6}. \]  

(c.iv-1)

The force, defined as the negative gradient of the potential, is:

\[ F = -|\vec{V}\vec{V}_{\text{disp}}(R)| = 6\frac{C_6}{R^7}\hat{R}. \]  

(c.iv-2)

For the London model of discrete distribution of charges, the total force is:

\[ \vec{F}_{\text{tot}} = \sum_i \vec{F}_i \]  

(c.iv-3)

where:

\[ \vec{F}_i = 6\frac{(C_6)_{\text{v}}}{R_i^7}\hat{R}_i \]  

(c.iv-4)

is the force arising from each charge. For the interaction between a point and a continuous distribution of charges, the summation converts to an integral over the surface and the total force is

\[ F = \int_S d\vec{F}. \]  

(c.iv-5)

\( d\vec{F} \) is the force between the point and a small element of the charge distribution where

\[ d\vec{F} = 6\frac{dC_6}{R^7}\hat{R}. \]  

(c.iv-6)

If an atom is described as a uniformly polarized spherical shell with total surface area \( A \), then \( d\vec{F} \) represents the interaction between a point and a small patch (with area \( dA \)) distance \( \rho \) away. This system is shown in Diagram (c.iv-1).

Since the dispersion coefficient is proportional to the polarizability of a uniformly polarizable shell, \( dC_6 \) will be a fraction of \( C_6 \) that can be expressed as:
\[
dC_6 = C_6 \frac{dA}{A}. \tag{c.iv-7}
\]

In (c.iv-7), \(dA = r^2 \sin \theta d\theta d\phi\) and \(A = 4\pi r^2\). Note that

\[
C_6 = \oint dC_6 = C_6 \frac{1}{A_s} \oint dA. \tag{c.iv-8}
\]

Equation (c.iv-5) can then be written as:

\[
F = \left[ \oint \frac{6}{\rho^2} \frac{dC_6}{\rho^7} \rho \right] = \left[ \int \frac{6}{\rho^2} \frac{C_6 r^2 \sin \theta d\theta d\phi}{4\pi r^2} \rho \right] \tag{c.iv-9}
\]

Note that as the force is integrated over \(\phi\), at \(\phi = 180^\circ\), there will be a vector force with \(dA'\) such that the net force between these two patches will be along the internuclear distance. That is, the perpendicular components of each vector force will cancel. This is shown in Diagrams (c.iv-2) and (c.iv-3).
To express this mathematically, the net force vector will be in the direction of \( \hat{\tau} \) to give

\[
dF_i = dF \cos \beta. \tag{c.iv-10}
\]

The total force can now be expressed as

\[
F = \int_0^\theta \int_0^{2\pi} 6C_s \frac{r^2 \sin \theta \, d\theta \, d\phi}{4\pi r^2} \cos \beta \hat{\tau}. \tag{c.iv-11}
\]

In (c.iv-11), \( \cos \beta \) can be written as:

\[
\cos \beta = \frac{\text{adjacent}}{\text{hypotenuse}} = \frac{r - r \cos \theta}{\rho} \tag{c.iv-12}
\]

and from the cosine rule,

\[
C^2 = A^2 + B^2 - 2AB \cos \gamma, \tag{c.iv-13}
\]

where \( A, B, \) and \( C \) are the legs of a triangle and \( \gamma \) is the angle between legs \( A \) and \( B \), \( \rho \) can be expressed as

\[
\rho = (r^2 + \tau^2 - 2r \tau \cos \theta)^{1/2}. \tag{c.iv-14}
\]

Substituting (c.iv-14) into (c.iv-12) and substituting this expression into (c.iv-11) will give

\[
F = \int_0^\theta \int_0^{2\pi} 6C_s \frac{\tau - r \cos \theta}{(r^2 + \tau^2 - 2r \tau \cos \theta)^{3/2}} \sin \theta \, d\theta \, d\phi \hat{\tau}. \tag{c.iv-15}
\]

Evaluating this integral will give

\[
F = C_s \frac{2 \tau (5r^2 + 3\tau^2)}{3(r^2 - \tau^2)^3}. \tag{c.iv-16}
\]

The potential energy of the system can be calculated by taking the negative integral of (c.iv-16):

\[
V^{\text{disp}}(\tau) = -\int F \, d\tau, \tag{c.iv-17}
\]
to give:

\[
V(\tau) = -C_6 \frac{r^2 + \tau^2}{(r^2 - \tau^2)^2} = -\frac{C_6}{(r^2 - \tau^2)^2} \frac{r^2 + \tau^2}{\tau^2 - r^2}.
\]  

(c.iv-18)

It is seen that the potential between a point and a spherical shell is reminiscent of the London model in that the total potential depends on \(\tau^6\) where \(\tau = R\) for this case. The next step is to describe a spherical atom interacting with another spherical atom.

- **Spherical shell-spherical shell model**

  The interaction can first be thought to consist of a small area element \(dA_1\) on sphere 1 (with radius \(r_1\)) with small area element \(dA_2\) on sphere 2 with radius \(r_2\) (shown in (Diagram c.iv-4)). The force again will be:

  \[
  F = \int \frac{dC_6}{\rho^2} \hat{\rho}
  \]  

  (c.iv-19)

  except this time, \(dC_6\) will depend on both spherical shell 1 and spherical shell 2. Thus, \(dC_6\) is equal to:

  \[
dC_6 = C_6 \frac{dA_1}{A_1} \frac{dA_2}{A_2}
  \]  

  (c.iv-20)

  ![Diagram](c.iv-4)

  The force will be an integral over surface 1 and surface 2:
Starting with surface 1, the integral over \( S_1 \) simplifies because the perpendicular vector components cancel similarly to the point-sphere case. This is shown in Diagram (c.iv-4). Using the calculations from the previous section, (c.iv-21) can be written as:

\[
F = \left| 6C_s \int_{s_1} \frac{r_i^2 \sin \theta_i \, d\theta_i \, d\phi_i}{4\pi r_i^2} \int_{s_1} \frac{1}{\rho} \frac{r_i^2 \sin \theta_i \, d\theta_i \, d\phi_i}{4\pi r_i^2} \right|. \tag{c.iv-21}
\]

\[
\int_{s_1} \frac{r_i^2 \sin \theta_i \, d\theta_i \, d\phi_i}{4\pi r_i^2} \int_{s_1} \frac{1}{\rho} \frac{r_i^2 \sin \theta_i \, d\theta_i \, d\phi_i}{4\pi r_i^2}.
\]

Equation (c.iv-23) shows that when the force between the small area elements on sphere 2 with sphere 1 is evaluated, the net interaction of all the dA2’s will be with the center of sphere 1. Evaluating the integral over surface 2, the perpendicular vector component of each force will cancel to give a net force that is along the internuclear axis (shown in Diagram c.iv-5 and c.iv-6).

So for:

\[
d\bar{F} = \frac{r_i^2 \sin \theta_i \, d\theta_i \, d\phi_i}{4\pi r_i^2} \frac{2\tau(5r_i^2 + 3\tau^2)}{3(r_i^2 - r_1^2)^3} \hat{t}, \tag{c.iv-24}
\]

the net force vector will be:

\[
d\bar{F}_n = d\bar{F}\cos\alpha. \tag{c.iv-25}
\]

Where:
Using the Cosine rule, \( \tau \) can be expressed as:

\[
\tau = (R^2 + r_2^2 - 2Rr_2\cos\theta_2)^{1/2}
\]

(c.iv-27)

to give the force to be:

\[
F = \left[ \frac{2(R - r_2\cos\theta_2)(5r_2^2 + 3(R^2 + r_1^2 - 2Rr_1\cos\theta_2))}{3((R^2 + r_1^2 - 2Rr_1\cos\theta_1) - r_1^2)^3} \cdot \frac{1}{4\pi} \sin\theta_2 d\theta_2 dr_2 R \right].
\]

(c.iv-28)

Solving the integral will give:

\[
F = -C_s \left[ \frac{r_1^4 - 2(5R^2 + 4r_1R - r_1^2)r_2^4}{24R^2 r_2(r_1^2 + (R + r_1)^2)} \cdot \frac{r_2^4 + 2(-5R^2 + 4r_1R + r_1^2)r_2^4}{24R^2 r_2(r_1^2 + (R - r_1)^2)} \cdot 3(R - r_1)^2(5R - r_2)^2 \right].
\]

(c.iv-29)

Finding the negative integral of (c.iv-29) to calculate the potential gives:

\[
V^{\text{neg}}(R) = -C_s \frac{3r_1^4 - 3(R^2 + r_1^2)r_2^4 + (-3R^4 + 14R^2 r_1^2 - 3r_1^2)r_2^4 + 3(3R^2 - r_1^2)^3(R^2 + r_2^2)}{3(r_1^4 - 2(R^2 + r_1^2)r_2^4 + (R^2 - r_1^2)^3)}. \]

(c.iv-30)

To get a simpler equation, equation (c.iv-30) will be simplified as follows: if all the quantities in the denominator are factored out and regrouped, it can be written as

\[
3[(-R + r_1 - r_2)(R + r_1 - r_2)(-R + r_1 + r_2)(R + r_1 + r_2)]^3
\]

(c.iv-31)


\[
= 3[(R^2 - (r_1 + r_2)^2)^3(R^2 - (r_1 - r_2)^2)^3].
\]

(c.iv-32)
Substituting this expression into the denominator gives

\[ V_{\text{disp}}(R) = -\frac{C_6}{(R^2 - (r_1 + r_2)^2)^3} \left[ 1 + \frac{3(\tau^2_1 - 3r_1^2 + \tau^2_2)R^2 - 2(3\tau^2_1 - 9r_1^2 + 10r_2^2 - 9r_1^2r_2 + 3r_2^2)R^2 + 3(\tau_2 - r_2)^2(\tau_2^2 - 4r_1^2 - 4r_2^2 - \tau_1^2 - \tau_2^2)}{(R^2 - (r_1 + r_2)^2)^3} \right]. \]  

(c.iv-33)

The term outside the bracket looks very similar to the London model where the internuclear distance has \( R^6 \) dependence. The only difference is that the internuclear distance is decreased by the sum of the two spherical radii. This single quantity takes into account the continuous distribution of charges.

The term that multiplies to the \( C_6 \) term can be shown that it converges to one rapidly. That is, if \( \frac{3(R^2 - (r_1 - r_2)^2)^3}{3(R^2 - (r_1 + r_2)^2)^3} \) is added and subtracted such that effectively no operation is done to the term in the bracket of equation (c.iv-23), the equation simplifies to:

\[ V_{\text{disp}}(R) = -\frac{C_6}{(R^2 - (r_1 + r_2)^2)^3} \left[ 1 + \frac{3\tau^2_1 - 3(r_1^2 + \tau_2^2)R^2 + 3(\tau_2 - r_2)^2(\tau_2^2 + r_2^2)}{(R^2 - (r_1 + r_2)^2)^3} \right]. \]

This can be written to its final form as:

\[ V_{\text{disp}}(R) = -\frac{C_6}{(R^2 - (r_1 + r_2)^2)^3} \left[ 1 + \frac{3(\tau_2^2 - 3r_2^2 + \tau_2^2)R^2 - 2(3\tau_1^2 - 9r_1^2 + 10r_2^2 - 9r_1^2r_2 + 3r_2^2)R^2 + 3(\tau_2 - r_2)^2(\tau_2^2 - 4r_1^2 - 4r_2^2 - \tau_1^2 - \tau_2^2)}{(R^2 - (r_1 + r_2)^2)^3} \right]. \]

or as

\[ V_{\text{disp}}(R) = -\frac{C_6}{(R^2 - (r_1 + r_2)^2)^3} \left[ 1 + \delta \right]. \]  

(c.iv-34)
For the case where \( r_1 = r_2 = r \), the potential simplifies to:

\[
V^\text{disp}(R) = -\frac{C_6}{(R^2 - (2r)^2)} \left[1 - \frac{2r^2}{3R^2}(3 - \frac{4r^2}{R^2})\right].
\]  
(c.iv-35)

From the (c.iv-33) and (c.iv-35), the leading term for \( \delta \) dies off as \( R^{-2} \) and will converge to zero. Thus for \( R > r_1, r_2 \), the term in the bracket will be insignificant and can be ignored.

The final form of the spherical atom model can now be expressed as

\[
V^\text{disp}(R) = -\frac{C_6}{(R^2 - (r_1 + r_2)^2)^{1/3}}.
\]  
(c.iv-36)

**C.v Spherical atom model damping function**

Similar to the London model, the spherical atom model also does not take into account density overlap and overestimates the dispersion energy. A new damping function for the spherical atom model will be developed to correct this behavior.

To subtract off the dispersion energy the spherical atom attributes to the overlapping portion of the spheres, the Coulomb \( 1/R \) potential of a point charge and a sphere is considered first.

In order to calculate the potential energy of this system, the electric field of a polarized spherical shell is calculated. The Gauss’ law states that the flux of the electric field through a spherically symmetric Gaussian surface is:

\[
\oint_S \nabla \cdot \vec{E} \cdot d\vec{a} = \int_S \frac{\theta}{4\pi\varepsilon_0 r^2} r^2 \sin \theta d\theta d\phi = \frac{q}{\varepsilon_0}.
\]  
(c.v-1)

Using this relationship, the electric field outside the spherical shell can be calculated from:
to give the electric field outside and inside the shell as:

\[
\vec{E} = \frac{q}{4\pi\varepsilon_0 R^2} \hat{R} \quad R>r \tag{c.v-3a}
\]

\[
\vec{E} = \frac{q}{4\pi\varepsilon_0 R^2} \hat{R} = 0 \quad R<r \tag{c.v-3b}
\]

From (c.v-3b), the electric field inside the shell is zero because all the charges are on the surface of the shell.

The potential is calculated next where the potential is defined to be:

\[
V(r) = \int \vec{E} \cdot d\vec{r} \quad \text{or} \quad \vec{E} = -\nabla V \tag{c.v-4}
\]

with respect to a given reference point. The potential outside the shell is:

\[
V(R) = -\frac{1}{4\pi\varepsilon_0} \int \frac{q}{R^2} dR' = \frac{1}{4\pi\varepsilon_0} \frac{q}{R} \tag{c.v-5}
\]

The potential inside the shell is evaluated from:

\[
V(R) = -\int_{\infty}^{R} \vec{E}(\text{outside shell}) \cdot d\vec{R}' - \int_{0}^{R} \vec{E}(\text{inside shell}) \cdot d\vec{R}' \tag{c.v-6}
\]

\[
V(R) = \frac{1}{4\pi\varepsilon_0} \frac{q}{R^2} dR' = \frac{1}{4\pi\varepsilon_0} \frac{q}{r} \tag{c.v-7}
\]

where the reference point is at infinity. Quantum mechanically treating this problem, the potential energy difference for a point inside and outside a shell can be calculated by evaluating:

\[
< U(R > r) > - < U(R < r) > \tag{c.v-9}
\]

\[
= < \psi(r) | U(R > r) | \psi(r) > - < \psi(r) | U(R < r) | \psi(r) > \tag{c.v-10}
\]
The spherically symmetric hydrogen 1s wavefunction:

\[ \psi_{1s} = \frac{1}{\sqrt{\pi}} \exp(-r), \quad (c.v-13) \]

will be used to describe the atoms.

Expression (c.v-10), explicitly written below,

\[ \int_0^{\frac{\pi}{2}} \int_0^{\frac{\pi}{2}} \int_0^{\infty} e^{-r^2} r^2 \sin \theta \sin \phi \sin \theta \sin \phi \, dr \, d\theta \, d\phi, \quad (c.v-14) \]

evaluates to be

\[ \frac{1 - e^{-R}}{R} \cdot \left[ 1 - (1 + R)e^{-2R} \right]. \quad (c.v-15) \]

For a Coulomb potential described by \(1/R\), the total fraction of potential due to nonoverlapping densities is given by (c.v-15). Carrying this idea over to dispersion potentials, if the dispersion potential is proportional to \(-1/R^6\), then the corrected dispersion potential will be

\[ V = -\frac{C_6}{R^6} \cdot \left[ 1 - (1 + R)e^{-2R} \right]. \quad (c.v-16) \]

The term in the bracket damps the dispersion potential. For the spherical atom model, the potential energy is:

\[ V = -\frac{C_6}{[R^2 - (r_1 + r_2)^2]^3} \cdot \left[ 1 - (1 + R)e^{-2R} \right]. \quad (c.v-17) \]

However, in the spherical atom model, when \(R=(r_1+r_2)\), the potential energy is undefined and goes off to negative infinity. The damping function is not zero at this point and shows that it damps too slowly. Although this damping function correctly damps the London model, for the spherical atom model, the internuclear distance needs to be shifted such that with a given radius \(r_d\), the damping function at \(R=2r_d\)
will be zero. That is, the function will be modified such that the overall spherical atom model and the damping function will be:

\[
V_{\text{disp}}(R) = -\frac{C_s}{[R^2 - (r_d + r_s)^2]^n} \left[ 1 - \left( \frac{R - 2r_s}{r_d} \right) \right] e^{-\frac{R - r_s}{r_d}}. \quad (c.v-18)
\]

The parameter \( r_d \) will be called the damping radius.

A full model describing dispersion energy is now developed and the spherical atom model with the new spherical atom damping function needs to be tested and compared to the London model with the Tang and Toennies damping function. However, before this is done, several \textit{ab initio} methods that will be used in Section E will be discussed in the next section.
D Computational Methods

As mentioned in Section B, the Schrödinger equation becomes unsolvable beyond one electron systems. Therefore, approximate methods are the only means to obtain information about these quantum mechanical systems. Methods that attempt to solve the Schrödinger equation without any experimental parameters are called \textit{ab initio} methods and some of these methods will be discussed here.

D.i Basis Sets

In order to construct a trial wavefunction, each electron is assigned to a single electron spin orbital called a molecular orbital. Each molecular orbital is defined in terms of atomic orbitals as:

$$\phi_i = \sum_{i=1}^{b} c_{i} \chi_{s}$$  \hspace{1cm} (d.i-1)

where this method is called linear combination of atomic orbitals (MO-LCAO). The atomic orbital, else called basis function, is usually a linear combination of Gaussian functions

$$\chi_{i} = \sum_{p} d_{i} g_{p} = \text{(CGTF)}$$  \hspace{1cm} (d.i-2)

where the Gaussian functions (called primitives) have the form:

$$g(\alpha, r) = cx^{m}y^{n}z^{l}e^{-ar}.$$  \hspace{1cm} (d.i-3)

The spherical harmonics are used to describe the angular component. When only one CGTF is used to represent the inner and outer atomic orbitals, the basis set is called a minimal basis set. An N-zeta basis set will have N CGTF’s to describe each
atomic orbital. A valence N zeta will use one CGTF for the inner orbitals and N CGTF’s for the valence orbitals.

From equation (b-8), the molecular orbitals should be described by a complete set of atomic orbitals. However, this is not feasible and using a finite number of functions introduces error that is called basis set truncation error (BSTE). To reduce this error, polarization basis functions that have one higher angular momentum than the highest occupied valence orbitals can be added to the basis set to allow the atomic orbitals to vary in shape and have more angular freedom. Inclusion of diffuse functions in one higher energy level than the valence orbitals will give a better description of the outer region of the atomic orbitals relative far from the nuclear centers. This function is especially important because it will compensate for the rapidly decaying behavior of the Gaussian functions (compared to the hydrogenlike radial exponential term).

The Dunning’s basis sets, aug-cc-pVNZ\textsuperscript{19}, will be discussed here. These basis sets are split N-zeta basis sets that include both polarization and diffuse functions for each valence atomic orbital. These basis sets were specifically developed to describe the dynamical correlation between electrons.

For dispersion interactions, large basis sets are required since the interactions arise not from sharing or exchanging electrons but from instantaneous correlation between electrons that occur at distances much farther out than covalent and ionic interactions. It has been found that using a practical size basis set on each nuclear center is not large enough to account for all of the dispersion energy\textsuperscript{20} and that diffuse and polarization functions are needed to describe the nonlocal interaction\textsuperscript{56}. 
Fortunately, adding a set of primitives in between the internuclear distances effectively describes a system calculated with a larger basis set. This method shows to be very efficient since it significantly reduces the computational time. These sets of primitives will be called bond functions and the primitive exponents will be optimized to give the lowest interaction energy.

**D.ii  Hartree Fock**

The Hartree Fock method is the first *ab initio* that will be discussed and the other methods will rely on the Hartree Fock results. In the Hartree Fock method, the electrons are represented as continuous charge distributions and the interelectronic Coulombic interaction is approximated by an effective potential that describes repulsion between overlapping charge densities.

The charge distribution of electron $j$ is expressed (in SI units for clarity) as

$$\rho_j = e |\phi_j|^2.$$  \hspace{1cm} (d.ii-1)

From the Slater determinant of molecular orbitals, an antisymmetrized wavefunction to describe the fermionic nature of electrons can be constructed:

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_j(x_1) & \ldots & \phi_N(x_1) \\ \phi_1(x_2) & \phi_j(x_2) & \ldots & \phi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(x_N) & \phi_j(x_2) & \ldots & \phi_N(x_N) \end{vmatrix}.$$  \hspace{1cm} (d.ii-2)

This trial function is the eigenfunction to a system with $N$ noninteracting electrons.

The Hamiltonian can be written in terms of one electron Fock operator where a Fock operator is expressed as:

$$\hat{F}(1) = \hat{H}^{\text{core}}(1) + \sum_j \hat{j}_j(1) - \hat{K}_j(1).$$  \hspace{1cm} (d.ii-3)
The first operator is the hydrogenlike Hamiltonian that contains the kinetic and the electron-nuclear attractive potential operator; $\hat{J}$ is the Coulomb operator that describes the repulsion between two electron clouds; $\hat{K}$ is the exchange operator that arises from the antisymmetry requirement.

The one electron energy can be expressed as

$$
\varepsilon_i = \langle \phi_i | \hat{H}^{\text{core}} | \phi_i \rangle = H_i^{\text{core}} + \sum_j \int \frac{\phi_i^*(1) \phi_j(2)}{r_{12}} \phi_i(1) dv_1 - \int \phi_i^*(1) \frac{\phi_j(2) \phi_j(1)}{r_{12}} \phi_i(2) dv_1 . \quad (\text{d.ii-4})
$$

In terms of basis functions (AO’s), the coulomb and the exchange integral for molecular orbital $i$ can be expressed as:

$$
\langle \phi_i | \hat{J}(1) | \phi_i \rangle = \sum_{j, t} \sum_{t, u} c_{i, t} \phi_{i, u} c_{j, u} \int \frac{\chi_{i, t}(1) \chi_{j, u}(1) \chi_{i, t}(2) \chi_{j, u}(2)}{r_{12}} dv_1 dv_i . \quad (\text{d.ii-5a})
$$

and as:

$$
\langle \phi_i | \hat{K}(1) | \phi_i \rangle = \sum_{j, t} \sum_{t, u} c_{i, t} \phi_{i, u} c_{j, u} \int \frac{\chi_{i, t}(1) \chi_{j, u}(1) \chi_{i, t}(2) \chi_{j, u}(2)}{r_{12}} dv_1 dv_i . \quad (\text{d.ii-5b})
$$

The $H_i^{\text{core}}$ energy can similarly be written as

$$
\langle \phi_i | \hat{H}_i^{\text{core}} | \phi_i \rangle = \sum_r \sum_s c_{i, s} \chi_{i, s} \hat{H}_{s, r} \chi_{r, s} = \sum_r \sum_s c_{i, s} \chi_{i, s} \hat{H}_{rs} \chi_{r, s} . \quad (\text{d.ii-5c})
$$

In general, the molecular orbital energy given in (d.ii-4) is solved self-consistently. That is, each one electron energy can be optimized by first considering the one electron equation:

$$
\sum_s c_{s, i} \hat{\chi}_{s, i} = \varepsilon_i \sum_s c_{s, i} \chi_{s, i} \quad (\text{d.ii-6})
$$

By taking the dot product with $\chi_r$, (d.ii-6) can be rewritten as:

$$
\sum_s c_{s, i} (F_{rs} - \varepsilon_i S_{rs}) = 0 \quad (\text{d.ii-7})
$$
where \( S_{rs} \) is the overlap integral. Equation (d.ii-7) forms a set of equations where the solution is the solution to the secular equation given below:

\[
\det(F_{rs} - \epsilon_i S_{rs}) = 0
\]  

(d.ii-8)

The roots to equation (d.ii-8) will be the MO orbital and this variational energy can be used to solve the coefficients in the MO-LCAO. The process is repeated until the energy and the wavefunction are relatively converged. The final Hartree Fock energy of the system will be the sum of all Fock or MO energies.

- **Comment**

  In the Hartree Fock method, because the interelectronic repulsion energy is smoothed out into an effective Coulomb and exchange potentials\(^{23}\), the instantaneous correlated motions of electrons to avoid each other are neglected. This introduces an inherent error in the SCF method and is called correlation energy.

  Methods to add in correlation effects will be described in the next sections and the total energy of the system will be represented as:

\[
E = E_{\text{HF}} + E_{\text{Corr}}
\]

(d.ii-9)

For interactions between nonpolar species, the Hartree Fock energy will be purely repulsive\(^{30}\) and the correlation energy will be the dispersion energy.

**D.iii MPn’s - Many Body Perturbation Theory (MBPT)**

The Møller Plesset method\(^{25}\) is based on the perturbation theory where the unperturbed Hamiltonian is the sum of the one electron Fock operator and the unperturbed wavefunction is the Hartree Fock wavefunction. The perturbation will
be the difference between the true interelectronic repulsion and the Hartree Fock effective repulsion:

\[ \hat{H}^{(1)} = \hat{H} - \hat{H}^{(0)} = \sum_i \sum_{j \neq i} \frac{1}{r_{ij}} - \sum_i \sum_{j \neq i} \hat{J}(j) - \hat{K}(j) \]  

The dynamic correlation between electrons can be represented by exciting electrons to unoccupied orbitals (else called virtual orbitals), so that the electrons are better able to spatially avoid each other. Including all possible orders of excitations (configuration interaction) will obtain the best correlation energy calculation possible for the given number of basis functions. However, considering all possible types of electronic configuration is demanding and the \textit{ab initio} method that includes more excited configurations will be considered to be a better method.

For perturbation method, it has been shown that the first order correction to the energy and the wavefunction is zero\textsuperscript{25}. The second order perturbation can be expressed as:

\[ E^{(2)} = \sum_s \left| \left\langle \psi_s^{(0)} | H^{(1)} | \Phi_0 \right\rangle \right|^2 \]

where \( \Phi_0 \) is the Hartree Fock ground state configuration.

It has been shown that only double excitations have nonzero matrix elements. Thus, if a and b represent the virtual orbitals, (d.iii-2) can be rewritten as:

\[ E^{(2)} = \sum_{ij} \sum_{ab} \left| \left\langle ab | r^{-1} | ij \right\rangle \right|^2 \frac{1}{(\epsilon_i + \epsilon_j) - (\epsilon_a + \epsilon_b)} \]

or as:

\[ E^{(2)} = \sum_s \frac{V_{0s} V_{s0}}{E_0 - E_s} \]
where $s$ covers all double substitutions and $V_{0s}$ is the matrix element:

$$(s || 0) = (ab || ij) = (ab | r^{-1} | ij - ji) \quad \text{(d.iii-3c)}$$

Note that (d.iii-3) can also be written in terms of pair energies such that:

$$E^{(2)} = \sum_{j} e_{j}^{(2)} \quad \text{(d.iii-4a)}$$

where:

$$e_{j}^{(2)} = -\sum_{ab} \frac{|(ab || ij)|^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}. \quad \text{(d.iii-4b)}$$

The second order energy is important in that the correlation energy can be separated into intramolecular and intermolecular pair energies\textsuperscript{27}: the excitations from localized orbitals on one monomer will give the intramonomer correlation energy; the simultaneous excitations localized on different monomers will give the intermolecular correlation energy\textsuperscript{12}.

The third order energy also only accounts for double excitations and is expressed as

$$E^{(3)} = -\sum_{ij} \sum_{cd} \sum_{ab} (ab || ij)([(ab || cd) - E^{(0)}(ab || cd)](cd || ij)) \left[ (\epsilon_a + \epsilon_b - (\epsilon_i + \epsilon_j))[(\epsilon_c + \epsilon_d) - (\epsilon_i + \epsilon_j)] \right]. \quad \text{(d.iii-5a)}$$

or as:

$$E^{(3)} = \sum_{a} \frac{V_{a0}(V_{a1} - V_{00}\delta_{a})V_{10}}{(E_{a} - E_{1})(E_{a} - E_{i})} \quad \text{(d.iii-5b)}$$

where $s$ and $t$ represent the double excitation given in (d.iii-5a) and $\delta_{a}$ represent the matrix element $\langle ab | cd \rangle$ or $\langle s | t \rangle$.

The fourth order perturbation energy, MP4(SDTQ), takes into account single, double, triple, and quadruple excitations:
\[ E^{(4)} = E^{(4)}_S + E^{(4)}_D + E^{(4)}_T + E^{(4)}_Q. \]  
(d.iii-6a)

\[ E^{(3)} + \sum_{su} \sum_t \frac{S_{0s} (V_{ut} - V_{0u}) (V_{vt} - V_{0t}) V_{ut}}{(E_0 - E_t) (E_0 - E_t) (E_0 - E_u)}. \]  
(d.iii-6b)

The sum over \( t \) accounts for all singles, doubles, triples, and quadruple excitation.

The triple excitations describing the correlation between three electrons are the most time consuming (because of the large number of configurations needed) but are critical to describe correctly long range correlation \(^{29,31}\).

**D.iv Couple cluster**

The couple cluster\(^{32-33}\) method is an iterative method that differs from the MBPT method in that while the MBPT method only includes all excitation terms to finite order, the couple cluster method is an iterative method that includes selective excitation terms to all orders.

In the couple cluster (CC) method, the excited configurations are taken into account by:

\[ \psi_{cc} = e^{\hat{T}} \Phi_{0}^{SCF} \]  
(d.vi-1)

where Taylor expansion of (d.vi-1) gives:

\[ \psi = \left[ 1 + \hat{T} + \frac{1}{2!} \hat{T}^2 + \frac{1}{3!} \hat{T}^3 + \frac{1}{4!} \hat{T}^4 + \ldots \right] \Phi_{0}^{SCF}. \]  
(d.vi-2)

\( \hat{T} \) is the cluster operator that is written as a sum of one-body to \( n \)-body operators:

\[ \hat{T} = \hat{T}_1 + \hat{T}_2 + \ldots + \hat{T}_n \]  
(d.vi-3)

If the cluster operator is truncated at the two-particle excitation operator, then the method is called CCSD. Because of the exponential nature of the operator, it can be seen that:
\[ e^{\hat{T}_1 + \hat{T}_2} \Phi_{\text{SCF}}^0 = (\hat{T}_1 + \hat{T}_2)\Phi_{\text{SCF}}^0 + \frac{1}{2}(\hat{T}_1 + \hat{T}_2)^2 \Phi_{\text{SCF}}^0 + \frac{1}{3!}(\hat{T}_1 + \hat{T}_2)^3 \Phi_{\text{SCF}}^0 + \ldots \] (d.iv-4a)

\[ = (\hat{T}_1 + \hat{T}_2)\Phi_{\text{SCF}}^0 + \frac{1}{2}(\hat{T}_1^2 + 2\hat{T}_1\hat{T}_2 + \hat{T}_2^2)\Phi_{\text{SCF}}^0 + \frac{1}{3!}(\hat{T}_1^3 + 3\hat{T}_1^2\hat{T}_2 + 3\hat{T}_1\hat{T}_2^2 + \hat{T}_2^3)\Phi_{\text{SCF}}^0 + \ldots \] (d.vi-4b)

CCSD effectively includes higher order excitations such as “disconnected” triple excitations (i.e., \( \hat{T}_1^2 \hat{T}_2 \), etc). Thus, the couple cluster method includes all orders of excitations.

When \( \hat{T}_1 \) operates on \( \Phi_{\text{SCF}}^0 \), a singly excited Slater determinant will be obtained:

\[ \hat{T}_1 \Phi_{\text{SCF}}^0 = \sum_{\text{occ}} \sum_{\text{unocc}} t_i^a \Phi_i^a \] (d.iv-5)

Likewise, \( \hat{T}_2 \) operating on \( \Phi_{\text{SCF}}^0 \) will give:

\[ \hat{T}_2 \Phi_{\text{SCF}}^0 = \sum_{ij} \sum_{ab} t_{ij}^{ab} \Phi_{ij}^{ab} \] (d.vi-6a)

Disconnected double excitation such as \( \hat{T}_2^2 \) on \( \Phi_{\text{SCF}}^0 \) will give

\[ \hat{T}_2^2 \Phi_{\text{SCF}}^0 = \sum_{ij} \sum_{abcd} t_{ij}^{abcd} \Phi_{ij}^{abcd} . \] (d.vi-6b)

The \( t_i^a \), \( t_{ij}^{ab} \), and \( t_{ij}^{abcd} \) are the amplitudes that select the terms from the expansion to be included in the configuration.

The CCSD energy can be written as

\[ E_{\text{CCSD}} = E_{\text{HF}} + \sum_{\text{occ}} \sum_{\text{unocc}} t_i^a (a | i) + \sum_{\text{occ}} \sum_{\text{unocc}} (ab || ij)(t_{ij}^{ab} + t_i^a t_j^b - t_i^a t_j^b) . \] (d.iv-7)

Calculating CCSDT energy that includes the “connected” triple excitations is an iterative process that is time consuming. Adding in the perturbative triples for the couple cluster triples proves to be an efficient and an accurate estimation. The
energy calculated from this method will be called CCSD(T) and will be expressed as:

\[
E_{\text{CCSD(T)}} = E_{\text{CCSD}} + \sum_{\alpha \neq \alpha'} \sum_{\gamma \neq \gamma'} \sum_{\alpha = \alpha'} \sum_{\gamma = \gamma'} \frac{t_{\alpha \gamma} V_{\alpha \gamma} t_{\alpha' \gamma'}}{E_{\alpha} - E_{\alpha'}}
\]  

(d.iv-8)

\[\text{Counterpoise Correction}\]

From the supermolecular approach, the interaction energy of the dimer system AB can be calculated by:

\[
\Delta E^\text{int}(R) = E_{\text{AB}}(R, \chi_{\text{AB}}) - [E_A(R, \chi_A) - E_B(R, \chi_B)]
\]  

(d.v-1)

where AB is calculated using basis set \(\chi_{\text{AB}} = \chi_A + \chi_B\), and each monomer A and B is calculated using \(\chi_A\) and \(\chi_B\) basis sets respectively. Ideally, the basis set for each component in (d.v-1) needs to be complete and extend over all space. However, these basis sets are finite and error arises where monomers A and B only have its own monomer basis sets available while A and B in the complex AB have both monomer basis sets available. The complex is overstabilized producing basis set superposition error (BSSE).

The Boys and Bernardi counterpoise correction\(^{35}\) is the most widely used method to correct for BSSE where the interaction energy is calculated by:

\[
\Delta E^\text{int}(R) = E_{\text{AB}}(R, \chi_{\text{AB}}) - [E_A(R, \chi_{\text{AB}}) - E_B(R, \chi_{\text{AB}})]
\]  

(d.v.-2)

This method will give each monomer equal amount of flexibility as the monomers in the dimer. Because dispersion is the most sensitive to the basis set used\(^{20}\), the counterpoise correction will be critical to obtain accurate potential energy surfaces.
D.vi  Comment: Density Functional Theory

One of the goals of the spherical atom model is to incorporate dispersion into density functional theory which graduate student Amy Austin\(^1\) has worked on. DFT was introduced by Hohenberg and Kohn\(^{37}\) who proved that the electronic energy depends only on the total electronic density\(^{55}\):

\[
E = \int \varepsilon(\rho(\tau))d\tau. \tag{d.iv-1}
\]

Consequently, the average energy of the system can be written as a functional:

\[
E[\rho_0] = \mathcal{T}[\rho_0] + \nabla_{\text{Ne}}[\rho_0] + \nabla_{\text{xc}}[\rho_0] \tag{d.vi-2}
\]

where each of the term describes the electron kinetic energy, the electron-nuclear attraction, and the electron-electron repulsion potential. The form of the density, however, is unknown and has to be solved variationally.

In 1965, Kohn and Sham\(^{38}\) introduced a systematic method to solve for the DFT energy and densities by first considering a system of noninteracting electrons each described by a one electron Kohn-Sham operator to give:

\[
h_{\text{KS}}^{\text{i}} = \epsilon_{\text{KS}}^{\text{i}} \tag{d.vi-3}
\]

The density can be calculated from:

\[
\rho = \sum_i |\theta_{\text{KS}}^{\text{i}}|^2. \tag{d.vi-4}
\]

The exact energy of the system can be written as

\[
E_0 = \sum_{\text{electrons}} \left\langle \theta_i | \nabla^2 | \theta_i \right\rangle + \sum_{\text{electrons}} \sum_{\alpha} \int \rho_{\alpha}^{\text{i}} \, d\tau + \sum_{\text{electrons}} \sum_{j} \int \rho_{j}^{\text{i}} \, d\tau d\tau_j + E_{\text{xc}}[\rho] \tag{d.vi-5}
\]

\[
= \bar{T}_{\text{i}}[\rho] + \bar{V}_{\text{i}}[\rho] + \bar{V}_{\text{Ne}}[\rho] + E_{\text{xc}}[\rho] \tag{d.vi-6}
\]

where the sum of

\[
\Delta \bar{T}[\rho] = \bar{T}[\rho] - \bar{T}_{\text{i}}[\rho] \tag{d.vi-7}
\]
\[ \Delta \nabla_{ee}[\rho] = \nabla_{ee}[\rho] - \nabla_{ee}[\rho]_n = \nabla_{ee}[\rho] - \int \frac{\rho(r)\rho(r')}{\eta_2} \, dr \, dr' \]  

(d.vi-8)

is the exchange-correlation energy, \( E_{xc} \). The terms designated with subscript \( s \) in (d.vi-7) and (d.vi-8) are the sum of the one electron energies evaluated from (d.vi-3). Theoretically, (d.vi-5) obtains the exact energy. However, the exact functional form of the exchange-correlation functional is unknown and some of the proposed models will be discussed below.

Two of the approximate methods are the LDA,

\[ E_{xc}[n] = \int n(r)\epsilon_{xc}(n(r)) \, dr , \]  

(d.vi-9)

and the LSDA method where these local density approximations describes electrons to move in \textit{jellium} or a “hypothetical electrically neutral, infinite-volume system consisting of an infinite number of interacting electrons moving in a space throughout which positive charge is continuously and uniformly distributed\(^2\).” The electrons in this \textit{jellium} constitute a homogeneous or a uniform electron gas. For systems with slowly varying densities, this approximation will be exact. However, in the region of overlapping densities or in regions near atomic nuclei, this approximation will fail.

The next method is the GGA method where the density gradient is included in the functional form to describe slowly changing densities.

\[ E_{xc}^{GGA}[\rho] = \int \epsilon_{xc}^{GGA}(\rho, \nabla \rho) \, dr \]  

(d.vi-10)

It can be shown that the exchange-correlation functional can be written as:

\[ E_{xc}(\rho) = E_X(\rho) + E_C(\rho) , \]  

(d.vi-11)
Some of the commonly used exchange functionals are the Axel Becke’s Bx86\textsuperscript{39, 40}, and Perdew and Wang’s PWx86\textsuperscript{41} and PWx91\textsuperscript{42}. Some of the common correlation functional used are Lee, Yang, and Parr’s LYP functional\textsuperscript{43} and Perdew’s Pc86 and Pc91 functionals\textsuperscript{44}.

Although DFT shows improvement over HF\textsuperscript{46} (since it includes some correlation), the methods described above are localized methods\textsuperscript{45} and fail to include long range (dispersion) interaction since they do not include simultaneous densities at two points.\textsuperscript{47-49, 55} For dispersion, it is necessary that

\[-\frac{C_6}{R_1^6} \sim g_6[p(r_1), p(r_2)]\]  

(d.vi-12)

Many attempts have been made to incorporate the damped London model to DFT\textsuperscript{50-51}. Amy Austin and Professor George Petersson showed that the spherical atom model can be added successfully to the density functional theory to give very good predictions of various interaction potentials.
E  Results I: Atomic Systems

In this section, the spherical atom model will be tested on the homonuclear and heteronuclear noble gas systems and on the \( \text{H}_2 \, ^3\Sigma_u \), \( \text{C}_2 \, ^9\Sigma_g \), and \( \text{HC} \, ^5\Sigma \) systems. Questions will arise as to which set of \( C_6, r_s, \) and \( r_d \) parameters are optimal to use and how these parameters should be developed and assigned to the atoms.

The spherical symmetry built into the spherical atom model will limit the types of systems to test to have isotropic electron density.

E.i  Noble gas systems

The noble gas systems are considered here to be the ideal systems to study dispersion interactions. The fully occupied valence shells make these atoms spherically symmetric and relatively stable. Dispersion will be the only attraction in these systems to bring these monomers to a bound state. For the noble gas systems (as well as other atomic systems), different sets of parameters will be assigned to each atom for the homonuclear diatomic complexes and the validity for each set will be evaluated in the heteronuclear systems.

E.i.a  He-He, Ne-Ne, Ar-Ar

The process of atom parameterization will heavily depend on the quantitative accuracy of the reference potential energy curves. All the reference curves discussed here will be developed from \textit{ab initio} calculations where a high level of calculation is needed such that adding higher order excitations and increasing the number of basis functions will not produce significant changes in energy. It is critical to have
converged energy values since the magnitude of these dispersion attractions will be very small.

This prerequisite demands for significant computational times, especially for systems containing big atoms such as argon. For efficiency, results from two references are used: for He-He, the authors of reference 52 estimated the FCI/CBS energies at every 0.25Å interval; for Ne-Ne and Ar-Ar, reference 53 gives CCSD(T)/aug-cc-pV5Z energies along the potential energy curve. Authors of reference 53 also includes optimized 3s3p2d2f1g mid-bond functions to reduce the basis set truncation error. These potential energy curves are given in Figure (e.ia-1) and the tabulated properties are given in Table (e.ia-1).

Before parameters are developed, the reference curves can be analyzed to predict the general trend for all three parameters in the spherical atom model. From section C, $C_6$ was shown to be proportional to the product of the polarizabilities. As the size of the atoms gets larger, the electron-nuclear Coulomb attraction decreases due to the increased electron-nuclear distance and increased inner-electron shielding. This will make the outer valence electrons more subject to attraction to the nearby nucleus, making the magnitude of the polarizability larger. The dispersion coefficient will consequently be larger for bigger atoms.
The internuclear distance at which the interaction energy is zero represents the distance at which the system is dominated by repulsion. The damping radius is connected to this point in that the correlation energy is expected to be zero when R is significantly less than this distance. Since the helium dimer system is characterized by the smallest \( R_{v=0} \) (and Ar-Ar the largest), the damping radius is expected to increase from He-He to Ar-Ar. The spherical atom radius represents the radius of the atom and is expected to follow this trend as well.

The parameters obtained for He-He, Ne-Ne, and Ar-Ar systems are given in Table (e.ia-2a) and Table (e.ia-2b). In Table (e.ia-2a), the well-known literature \( C_6 \) coefficients were used to simultaneously fit the \( r_s \) and \( r_d \) values. For Table (e.ia-2b), all three parameters were simultaneously nonlinear least squares fit to the reference curves. The first set of parameters will be labeled set 1 and the second set of parameters will be labeled set 2.

<table>
<thead>
<tr>
<th>Parameters/System</th>
<th>He-He</th>
<th>Ne-Ne</th>
<th>Ar-Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_6 )</td>
<td>1.46098</td>
<td>6.28174</td>
<td>63.752</td>
</tr>
<tr>
<td>( r_s )</td>
<td>0.9773±0.0011</td>
<td>1.2111±0.0031</td>
<td>1.4858±0.0020</td>
</tr>
<tr>
<td>( r_d )</td>
<td>1.353±0.002</td>
<td>1.6138±0.0032</td>
<td>1.6543±0.0192</td>
</tr>
</tbody>
</table>

**TABLE e.ia-2a:** \( r_s \) and \( r_d \) nonlinear least square fit parameters for He\(_2\), Ne\(_2\), and Ar\(_2\). This set will be called set 1.

<table>
<thead>
<tr>
<th>Parameters/System</th>
<th>He-He</th>
<th>Ne-Ne</th>
<th>Ar-Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_6 )</td>
<td>1.4231±0.0031</td>
<td>5.9046±0.0818</td>
<td>67.27±0.40</td>
</tr>
<tr>
<td>( r_s )</td>
<td>1.0256±0.0029</td>
<td>1.317±0.023</td>
<td>1.4472±0.0044</td>
</tr>
<tr>
<td>( r_d )</td>
<td>1.3846±0.0026</td>
<td>1.6733±0.01343</td>
<td>1.6714±0.0124</td>
</tr>
</tbody>
</table>

**TABLE e.ia-2b:** \( C_6, r_s, \) and \( r_d \) nonlinear least square fit parameters for He\(_2\), Ne\(_2\), and Ar\(_2\). This set will be called set 2.
Comparing the two sets, set 2 dispersion coefficients are smaller than those of set 1. For set 1, the coefficients are from reference 53 where the authors fit the parameters to the empirical potential:

$$V(R) = A \exp(-\alpha R + \beta R^2) + \sum_{n=3}^{8} f_2n(R; b) \frac{C_{2n}}{R^{2n}}.$$  

The exponential term in $V(R)$ has two parameters to reproduce the SCF repulsion curve; the second term is the London model that is damped by the Tang and Toennies damping function. The infinite expansion was truncated to six terms where all the terms lower than the $C_{12}$ term were fit to give values closest to the empirical estimates; the terms higher than the $C_{12}$ term were obtained from extrapolation. The authors had attempted to nonlinear least squares fit all parameters but had obtained unreasonable values (such as negative dispersion coefficients).

Because the $C_6$ values are smaller for set 2, the spherical atom radii are larger. It can be noted that the parameters are highly coupled to each other and will affect the nonlinear least squares fit. From the mathematics, if the dispersion coefficient is made larger, the spherical atom radius decreases and/or the damping radius decreases. Having more parameters to optimize makes the fit more complicated because there are more possible sets of values that will satisfy the fit convergence criteria. The uncertainties for the fit will increase. For set 2 (and set 1), since the uncertainties are only a small fraction of the optimized values, they will not make significant contributions and will be ignored.

Since the dispersion coefficients for the noble gases are well known, set 1 theoretically are the appropriate group of parameters to describe these systems. If a third parameter, $C_6$, does not significantly improve the fit, two parameters are better.
With the parameters developed, a fair method is required to compare the spherical atom model with the widely used London model. The biggest complication comparing the two models arises from the fact that these models use different damping functions. There is not yet a clear relationship between the two damping functions and for the most unbiased treatment possible, the multiplied damping correction will be excluded for the comparison.

The ratio of the spherical atom model to the reference curve and the same ratio with the multipole expansion with different number of terms are graphed in Figures (e.ia-3a-c) and Figures (e.ia-4a-c): Figures (e.ia-3) are from set 1 and Figures (e.ia-4a-c) are from set 2.

At short distances, as the electron densities start to overlap, it can be seen that all the models overestimate the attractive energy although the one-termed London model severely underestimates the dispersion energy to not show this trend. It can also be deduced that all the predictions will diverge to negative infinity. This behavior of all the models points out the importance of the damping functions to give physically reasonable non-diverging predictions and shows that the damping functions need to converge to zero as R decreases.

For the limit where the atoms are far from each other, all the models show the same effect: they all converge to the reference curves or near to the sum of the energies of two non-interacting atoms. This behavior is especially clear for the London model that was derived for long-range, non-overlapping densities interactions. The London model is the correct dispersion representation in this region and the spherical atom model should replicate this behavior. (Note that the spherical
atom model asymptotically resembles the London model). In this region, the damping function needs to approach one so that it has no damping effect on the system.

Comparing set 1 and set 2 predictions, set 2 predictions describe more correlation effects than set 1 for all three dimers. Also, set 1 curves converge much slower than set 2. If the spherical atom model is expanded, some of these behaviors can be explained.

To expand the spherical atom model, restated in (e.ia-1):

\[ V_{\text{dep}}(R) = -\frac{C_s}{R^6 \left[1 - \left(2\frac{r}{R}\right)^2\right]^3} = -\frac{C_s}{R^6 \left[1 - \left(2\frac{r}{R}\right)^2\right]^3}, \]  
\[ \text{(e.ia-1)} \]

\( \left(\frac{2r}{R}\right)^2 \) can be redefined as \( x \) to give:

\[ V_{\text{dep}}(R; x) = -\frac{C_s}{R^6 (1-x)^3} \]  
\[ \text{(e.ia-2)} \]

Since the power series expansion of \((1-x)^{-1}\) is represented by

\[ \sum_{n=0}^{\infty} x^n, \]  
\[ \text{(e.ia-3)} \]

differentiating \((1-x)^{-1}\) twice would give \(2(1-x)^{-3}\), which is also represented by differentiating the power series twice to give:

\[ \sum_{n=2}^{\infty} n(n-1)x^{n-2} = \sum_{n=0}^{\infty} (n+2)(n+1)x^n. \]  
\[ \text{(e.ia-4)} \]

So then, (e.ia-2) can be expanded into:

\[ V_{\text{dep}}(R; x) = -\frac{C_s}{R^6 \left(1 + 3x + 6x^2 + 10x^3 + 15x^4 + 21x^5 + \ldots\right)}. \]  
\[ \text{(e.ia-5)} \]

Equation (e.ia-5) can be rewritten as:

\[ V_{\text{dep}}(R) = -\frac{C_s}{R^6 \left(1 + \frac{4r}{R} + \frac{16r^2}{R^2} + \frac{32r^3}{R^3} + \frac{64r^4}{R^4} + \frac{128r^5}{R^5} + \ldots\right)} \]  
\[ \text{(e.ia-6a)} \]
Each term in the expanded spherical atom model resembles the multipole terms in the London model, indicating that representing atoms as polarizable spherical shells inherently includes multipole interactions beyond the dipole interaction. Equating the coefficient of each term in (e.ia-6b) to the respective dispersion coefficient, the predicted coefficients using set 1 and set 2 parameters are presented in Table (e.ia-4a) and Table (e.ia-4b). The literature values are given in Table (e.ia-3).

<table>
<thead>
<tr>
<th>Parameters/System</th>
<th>(\text{He}_2)</th>
<th>(\text{Ne}_2)</th>
<th>(\text{Ar}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_6)</td>
<td>1.46098</td>
<td>6.28174</td>
<td>63.7520</td>
</tr>
<tr>
<td>(C_8)</td>
<td>14.1179</td>
<td>90.0503</td>
<td>1.55646x10^3</td>
</tr>
<tr>
<td>(C_{10})</td>
<td>183.691</td>
<td>1.67945x10^3</td>
<td>4.94379x10^4</td>
</tr>
<tr>
<td>(C_{12})</td>
<td>3.26527x10^3</td>
<td>4.18967x10^4</td>
<td>2.07289x10^6</td>
</tr>
<tr>
<td>(C_{14})</td>
<td>7.64399x10^4</td>
<td>1.36298x10^6</td>
<td>1.105297x10^8</td>
</tr>
<tr>
<td>(C_{16})</td>
<td>2.27472x10^6</td>
<td>5.62906x10^7</td>
<td>7.24772x10^9</td>
</tr>
</tbody>
</table>

**TABLE e.ia-3**: Reference \(C_{2n}\).

<table>
<thead>
<tr>
<th>Mult. Coeff.</th>
<th>SAM Coeff.</th>
<th>(\text{He}_2)</th>
<th>(\text{Ne}_2)</th>
<th>(\text{Ar}_2)</th>
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</thead>
<tbody>
<tr>
<td>(C_6)</td>
<td>(C_6)</td>
<td>1.46098</td>
<td>6.28174</td>
<td>63.7520</td>
</tr>
<tr>
<td>(C_8)</td>
<td>12(C_6r_s^2)</td>
<td>16.74485</td>
<td>110.56590</td>
<td>2.14919x10^3</td>
</tr>
<tr>
<td>(C_{10})</td>
<td>96 (C_6r_s^4)</td>
<td>127.94611</td>
<td>1.29739x10^3</td>
<td>4.83020x10^4</td>
</tr>
<tr>
<td>(C_{12})</td>
<td>640 (C_6r_s^6)</td>
<td>814.68859</td>
<td>1.26864x10^4</td>
<td>9.04634x10^5</td>
</tr>
<tr>
<td>(C_{14})</td>
<td>3840 (C_6r_s^6)</td>
<td>4.66872x10^3</td>
<td>1.11648x10^5</td>
<td>1.52484x10^7</td>
</tr>
<tr>
<td>(C_{16})</td>
<td>21504 (C_6r_s^{10})</td>
<td>2.497137x10^4</td>
<td>9.17064x10^5</td>
<td>2.83989x10^8</td>
</tr>
</tbody>
</table>

**TABLE e.ia-4a**: Spherical atom model predicted higher order multipole terms using set 1.
<table>
<thead>
<tr>
<th>Mult. Coeff.</th>
<th>SAM Coeff.</th>
<th>He$_2$</th>
<th>Ne$_2$</th>
<th>Ar$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_6$</td>
<td>C$_6$</td>
<td>1.4231</td>
<td>5.9046</td>
<td>53.591</td>
</tr>
<tr>
<td>C$_8$</td>
<td>12C$_6$r$_s^2$</td>
<td>17.96274</td>
<td>122.89757</td>
<td>2.54057x10$^3$</td>
</tr>
<tr>
<td>C$_{10}$</td>
<td>96 C$_6$r$_s^4$</td>
<td>151.15367</td>
<td>1.70532x10$^3$</td>
<td>8.02933x10$^4$</td>
</tr>
<tr>
<td>C$_{12}$</td>
<td>640 C$_6$r$_s^6$</td>
<td>1.05994x10$^3$</td>
<td>1.97190x10$^4$</td>
<td>2.11468x10$^6$</td>
</tr>
<tr>
<td>C$_{14}$</td>
<td>3840 C$_6$r$_s^6$</td>
<td>6.68945x10$^3$</td>
<td>2.05214x10$^5$</td>
<td>5.01252x10$^7$</td>
</tr>
<tr>
<td>C$_{16}$</td>
<td>21504 C$_6$r$_s^{10}$</td>
<td>3.94035x10$^4$</td>
<td>1.99328x10$^6$</td>
<td>1.10892x10$^9$</td>
</tr>
</tbody>
</table>

TABLE e.ia-4b: Spherical atom model predicted higher order multipole terms using set 2.

One common point between set 1 and set 2 predictions is that both sets overestimate the second dispersion coefficients for all three systems and underestimate the others. For set 1, the slow convergence to the asymptotic limit can be attributed to this result: as R increases, the higher order terms will rapidly converge to zero as the inverse power of R increases. The C$_8$ term will be the second important term and overestimating this value will make the spherical atom model converge slower to the asymptotic limit. For set 2, this is not observed since the C$_6$ coefficient is smaller than the literature value.

Overall, the spherical atom model using set 1 and set 2 parameters is comparable to the London model with two or three terms, although this generalization does not hold for the argon dimer. For Ar-Ar, at short internuclear distances, the spherical atom model describes more correlation energy than the London model, indicating that the spherical atom damping function has a stronger effect on Ar-Ar than the two other systems and the Tang and Toennies damping function. The model
should give consistent results between these three systems and the necessity to
decouple the three parameters shows in the argon system.

\textit{E.i.b} \textit{He-Ne, He-Ar, Ne-Ar}

The parameters developed in the previous section represent the each atom and
the applicability to the heteronuclear systems will test the success of the spherical
atom model.

From equation (c.v-18), $r_s^{AB}$, the spherical atom radius is calculated from
adding the radius of atom A and atom B. The internuclear distance at which it is
twice the heteronuclear spherical atom radius will represent the point where the two
atomic shells are about to penetrate each other. The combination rules for the
dispersion coefficient and the damping radius are not as straightforward but it has
been shown that the geometric mean will give good results. Thus, these values can be
calculated by:

$$C_6^{AB} = \sqrt{C_6^{AA}C_6^{BB}}$$

and by:

$$r_d^{AB} = \sqrt{r_d^{AA}r_d^{BB}}.$$ 

The reference curves for He-Ne, He-Ar, and Ne-Ar are from reference 53
where the same \textit{ab initio} method used for the homonuclear dimers was used. The
reference curves are plotted in Figures (e.ib-1a) and (e.ib-1b). It is observed that He-
Ne shows the least attraction to each other and Ne-Ar dimer shows the most attraction
to each other.

Three parameter sets were tested: set 1a will consist of $C_6$, $r_s$, and $r_d$ values all
predicted from set 1 of the previous section; set 1b will use the literature dispersion coefficients for HeNe, HeAr, and NeAr and the predicted \( r_s \) and \( r_d \) values equivalent to set 1a; set 2a will use set 2 parameters to predict all three values. The predicted parameters are tabulated in Table (e.ib-1a) and Table (e.ib-1b). As a reference, the three parameters have been also fit to the reference curves and the values are tabulated in Table (e.ib-1c). The literature dispersion coefficients from reference 53 are given in Table (e.ib-4).

<table>
<thead>
<tr>
<th></th>
<th>HeNe</th>
<th>HeAr</th>
<th>NeAr</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_6 )</td>
<td>3.02943</td>
<td>9.65093</td>
<td>20.01183</td>
</tr>
<tr>
<td>( r_s )</td>
<td>1.0942</td>
<td>1.32425</td>
<td>1.44115</td>
</tr>
<tr>
<td>( r_d )</td>
<td>1.47765</td>
<td>1.61503</td>
<td>1.76383</td>
</tr>
</tbody>
</table>

**TABLE e.ib-1a:** Set 1a.

<table>
<thead>
<tr>
<th></th>
<th>HeNe</th>
<th>HeAr</th>
<th>NeAr</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_6 )</td>
<td>2.89876</td>
<td>8.82717</td>
<td>17.98039</td>
</tr>
<tr>
<td>( r_s )</td>
<td>1.1713</td>
<td>1.48485</td>
<td>1.63055</td>
</tr>
<tr>
<td>( r_d )</td>
<td>1.52212</td>
<td>1.71958</td>
<td>1.76383</td>
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</table>

**TABLE e.ib-1b:** Set 2a.

<table>
<thead>
<tr>
<th></th>
<th>HeNe</th>
<th>HeAr</th>
<th>NeAr</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_6 )</td>
<td>3.0854±0.07045</td>
<td>8.7294±0.0438</td>
<td>17.568±0.2077</td>
</tr>
<tr>
<td>( r_s )</td>
<td>1.0163±0.0406</td>
<td>1.4842±0.0085</td>
<td>1.6183±0.0198</td>
</tr>
<tr>
<td>( r_d )</td>
<td>1.4376±0.0211</td>
<td>1.7289±0.0063</td>
<td>1.8587±0.0143</td>
</tr>
</tbody>
</table>

**TABLE e.ib-1c:** Nonlinear least squares fit parameters.

<table>
<thead>
<tr>
<th></th>
<th>Reference value</th>
<th>Set 1a</th>
<th>Set 1b</th>
<th>Set 2a</th>
</tr>
</thead>
<tbody>
<tr>
<td>HeNe ( E_e )</td>
<td>-0.00006657</td>
<td>-0.00006976</td>
<td>-0.00007071</td>
<td>-0.00006993</td>
</tr>
<tr>
<td>Error</td>
<td>4.79%</td>
<td>6.21%</td>
<td>5.05%</td>
<td></td>
</tr>
<tr>
<td>HeAr ( E_e )</td>
<td>-0.00009415</td>
<td>-0.00009522</td>
<td>-0.00009039</td>
<td>-0.00009726</td>
</tr>
<tr>
<td>Error</td>
<td>1.14%</td>
<td>3.99%</td>
<td>3.30%</td>
<td></td>
</tr>
<tr>
<td>NeAr ( E_e )</td>
<td>-0.00020587</td>
<td>-0.00020867</td>
<td>-0.00019012</td>
<td>-0.0002101</td>
</tr>
<tr>
<td>Error</td>
<td>1.36%</td>
<td>7.65%</td>
<td>2.05%</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE e.ib-3:** Equilibrium energy predictions and error for set 1a, 1b, and 2a.
The predicted potential energy curves for each of the three systems using the three sets are graphed in Figure (e.ib-2a) to Figure (e.ib-2c). The predicted well depth errors are calculated in Table (e.ib-3).

The predictions given by the three sets of parameters mimic the reference potential relatively well. Set 1a and 2a gives the most accurate predictions for all three systems while set 1b gives larger errors for HeNe and NeAr.

For further evaluation, the dispersion coefficients can be predicted again from the spherical atom model Taylor expansion. The calculated values for the three sets are shown in Tables (e.ib-5a) to (e.ib-5c). Graphs shown in the homonuclear section are also plotted for HeNe, HeAr, and NeAr and are given in Figures (e.ib-3a) to (e.ib-3c), (e.ib-4a) to (e.ib-4c), and (e.ib-5a) to (e.ib-5c).

As with the homonuclear cases, the London model converges to the correct limit. That is, “all the points come together to one” as R gets larger. The spherical atom model using set 1a converges less rapidly than using set 1b except for HeNe. For HeNe, both sets show similar behavior since the predicted \( C_6 \) value and the literature coefficient are very similar to each other; furthermore, the same \( r_s \) value is used for the calculations. Analyzing predictions using set 2a, spurious behaviors are observed where the spherical model converges rapidly for NeAr, converges to the wrong limit for HeAr, and converges with set 1a and 1b for HeNe.
### Table e.ib-4: Parameters for the London model.

<table>
<thead>
<tr>
<th>Parameters/System</th>
<th>HeNe</th>
<th>HeAr</th>
<th>NeAr</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆</td>
<td>3.05239</td>
<td>9.38701</td>
<td>19.0098</td>
</tr>
<tr>
<td>C₈</td>
<td>31.6787</td>
<td>165.522</td>
<td>392.861</td>
</tr>
<tr>
<td>C₁₀</td>
<td>427.732</td>
<td>3.79716x10³</td>
<td>1.05627x10⁴</td>
</tr>
<tr>
<td>C₁₂</td>
<td>7.72516x10³</td>
<td>1.16518x10⁵</td>
<td>3.79879x10⁵</td>
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<tr>
<td>C₁₄</td>
<td>1.81945x10⁵</td>
<td>4.66258x10⁶</td>
<td>1.78160x10⁷</td>
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<tr>
<td>C₁₆</td>
<td>5.44012x10⁶</td>
<td>2.36861x10⁸</td>
<td>1.06075x10⁹</td>
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</tbody>
</table>

### Table e.ib-5a: The predicted multipole coefficients using set 1a.

<table>
<thead>
<tr>
<th>Multi.Coeff.</th>
<th>SAM C p.</th>
<th>HeNe</th>
<th>HeAr</th>
<th>NeAr</th>
</tr>
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<tbody>
<tr>
<td>C₆</td>
<td>C₆</td>
<td>3.02943</td>
<td>9.65093</td>
<td>20.01183</td>
</tr>
<tr>
<td>C₈</td>
<td>12C₆rₛ²</td>
<td>43.48424</td>
<td>203.09080</td>
<td>498.75413</td>
</tr>
<tr>
<td>C₁₀</td>
<td>96 C₆rₛ⁴</td>
<td>416.11207</td>
<td>2.84918x10³</td>
<td>8.28695x10³</td>
</tr>
<tr>
<td>C₁₂</td>
<td>640 C₆rₛ⁶</td>
<td>3.31824x10³</td>
<td>3.33096x10⁴</td>
<td>1.14742x10⁵</td>
</tr>
<tr>
<td>C₁₄</td>
<td>3840 C₆rₛ⁸</td>
<td>2.38148x10⁴</td>
<td>3.50477x10⁵</td>
<td>1.42985x10⁶</td>
</tr>
<tr>
<td>C₁₆</td>
<td>21504 C₆rₛ¹⁰</td>
<td>1.595232x10⁵</td>
<td>3.44181x10⁶</td>
<td>1.663024x10⁷</td>
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</tbody>
</table>

### Table e.ib-5b: The predicted multipole coefficients using set 1b.

<table>
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<th>Multi.Coeff.</th>
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<th>HeAr</th>
<th>NeAr</th>
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<td>19.0098</td>
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<tr>
<td>C₈</td>
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<td>C₁₀</td>
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<td>419.26462</td>
<td>2.77127x10³</td>
<td>7.87201x10³</td>
</tr>
<tr>
<td>C₁₂</td>
<td>640 C₆rₛ⁶</td>
<td>3.3433x10³</td>
<td>3.23986x10⁴</td>
<td>1.08997x10⁵</td>
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<tr>
<td>C₁₄</td>
<td>3840 C₆rₛ⁸</td>
<td>2.39952x10⁴</td>
<td>3.40893x10⁵</td>
<td>1.35826x10⁶</td>
</tr>
<tr>
<td>C₁₆</td>
<td>21504 C₆rₛ¹⁰</td>
<td>1.59523x10⁵</td>
<td>3.34769x10⁶</td>
<td>1.57975x10⁷</td>
</tr>
</tbody>
</table>
Overall, all three sets predict the potential energy curves within 10% accuracy and show that the three sets are valid in the chemically important region. Out of the three sets, however, using the literature homonuclear dispersion coefficients to predict the heteronuclear dispersion coefficients shows to be the best method.

<table>
<thead>
<tr>
<th>Mult.Coeff.</th>
<th>SAM Coeff.</th>
<th>HeNe</th>
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<th>NeAr</th>
</tr>
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<tbody>
<tr>
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<td>8.82717</td>
<td>17.98039</td>
</tr>
<tr>
<td>C₈</td>
<td>12C₆ᵣₛ²</td>
<td>47.72330</td>
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<td>C₁₀</td>
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<td>4.79074x10³</td>
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<td>3.94356x10⁴</td>
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<td>6.89975x10⁶</td>
</tr>
<tr>
<td>C₁₆</td>
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<td>3.02980x10⁵</td>
<td>9.88936x10⁶</td>
<td>5.13640x10⁷</td>
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</table>

TABLE e.ib-5c: The predicted multipole coefficients using set 2a.
He$_2$, Ne$_2$, and Ar$_2$ interaction energies

E$_{\text{inter}}$ (hartree a.u.)

Figure e.ia-1: The reference potential energy curves for He$_2$, Ne$_2$, and Ar$_2$. 
He$_2$, Ne$_2$, and Ar$_2$ correlation energies

Figure e.ia-2: Correlation energy curves for He$_2$, Ne$_2$, and Ar$_2$. 
He$_2$: Undampened Dispersion Models to FCI/CBS

Spherical atom model: $C_6 = 1.46098 + r_s^2 = 0.9773$

Figure e.ia-3a: He$_2$ correlation energy prediction analysis for the multipole expansion and the spherical atom model using parameters from set 1 ($C_6$=literature value; $r_s$ and $r_d$ nonlinear least squares fit).
\( \text{Ne}_2: \) Undamped Dispersion Model to CCSD(T)/aug-cc-pV5Z+3s3p2d1f

Spherical atom model: \( C_6 \): 6.28174 + \( r_s \): 1.2111

Figure e.ia-3b: \( \text{Ne}_2 \) correlation energy prediction analysis for the multipole expansion and the spherical atom model using parameters from set 1 (\( C_6 \)=literature value; \( r_s \) and \( r_d \) nonlinear least squares fit).
\( \text{Ar}_2 \): Undamped Dispersion Model to CCSD(T)/aug-cc-pV5Z+3s3p2d2f1g

Spherical atom model: \( C_6 = 63.752 + r_s = 1.6712 \)

Figure e.ia-3c: \( \text{Ar}_2 \) correlation energy prediction analysis for the multipole expansion and the spherical atom model using parameters from set 1 (\( C_6 = \) literature value; \( r_s \) and \( r_d \) nonlinear least squares fit).
He$_2$: Undamped Dispersion Model to FCI/CBS

Spherical atom model: $C_6: 1.4231 + r_s: 1.0256$

Figure e.ia-4a: He$_2$ correlation energy prediction analysis for the multipole expansion and the spherical atom model using parameters from set 1 ($C_6$, $r_s$, and $r_d$ nonlinear least squares fit).
Figure e.ia-4b: Ne$_2$ correlation energy prediction analysis for the multipole expansion and the spherical atom model using parameters from set 1 ($C_6$, $r_s$, and $r_d$ nonlinear least squares fit).
Figure e.ia-4c: \( \text{Ar}_2 \) correlation energy prediction analysis for the multipole expansion and the spherical atom model using parameters from set 1 \((C_6; r_s, \text{ and } r_d \text{ nonlinear least squares fit})\).
Heteronuclear noble gas dimer interaction energies set 1

\[
C_{AB}^{6} = (C_{6}^{AA}C_{6}^{BB})^{1/2}, \quad r_{s}^{AB} = (r_{s}^{AA} + r_{s}^{BB})/2, \quad r_{d}^{AB} = (r_{d}^{AA}r_{d}^{BB})^{1/2}
\]

HeNe E(CCSD(T)/aug-cc-pV5Z+3s3p2d2f1g)  
HeNe SAM*Damping+HF/aug-cc-pV5Z+3s3p2d2f1g  
HeAr E(CCSD(T)/aug-cc-pV5Z+3s3p2d2f1g)  
HeAr SAM*damping+HF/aug-cc-pV5Z+3s3p2d2f1g  
NeAr E(CCSD(T)/aug-cc-pV5Z+3s3p2d2f1g)  
NeAr SAM*damping+HF/aug-cc-pV5Z+3s3p2d2f1g

Figure e.ib-1a: Spherical atom model prediction for HeNe, HeAr, and NeAr using predicted $C_6$, $r_s$, and $r_d$ values from set 1.
Heteronuclear noble gas dimer interaction energies

\[ r_{s}^{AB} = \frac{r_{s}^{AA} + r_{s}^{BB}}{2} \]

\[ r_{d}^{AB} = \left( r_{d}^{AA} + r_{d}^{BB} \right)^{1/2} \]

\[ E_{\text{inter}} \text{(millihartree a.u.)} \]

Figure e.iib-1b: Spherical atom model prediction for HeNe, HeAr, and NeAr using literature C₆ values and predicted \( r_s \) and \( r_d \) values from set 1.
Figure e.ib-1c: Spherical atom model predictions for HeNe, HeAr, and NeAr using predicted $C_6$, $r_s$, and $r_d$ values using set 2.
HeNe: Undamped Dispersion Model to CCSD(T)/aug-cc-pV5Z+3s3p2d2f1g

Spherical atom model: $C_6 = 3.05239 + r_s = 1.09420$

Figure e.ib-2a: HeNe correlation energy prediction analysis for the multipole expansion and the spherical atom model using set1a parameters
HeAr: Undamped Dispersion Model to CCSD(T)/aug-cc-pV5Z+3s3p2d2f1g
Spherical atom model: $C_6 : 9.65093 + r_s : 1.32425$

Figure e.ib-2b: HeAr correlation energy prediction analysis for the multipole expansion and the spherical atom model using set1a parameters.
NeAr: Undamped Dispersion Model to CCSD(T)/aug-cc-pV5Z+3s3p2d2f1g
Spherical atom model: \( C_6 \cdot 20.01183 + r_s \cdot 1.44115 \)

Figure e.ib-2c: NeAr correlation energy prediction analysis for the multipole expansion and the spherical atom model using set1a parameters.
HeNe: Undamped Dispersion Model to CCSD(T)/aug-cc-pV5Z+3s3p2d2f1g

Spherical atom model: \( C_6: 3.02944 + r_s: 1.09420 \)

Figure e.ib-3a: HeNe correlation energy prediction analysis for the multipole expansion and the spherical atom model using set1b parameters.
HeAr: Undamped Dispersion Model to CCSD(T)/aug-cc-pV5Z+3s3p2d2f1g
Spherical atom model: \( C_6 : 9.38701 + r_s : 1.32425 \)

Figure e.ib-3b: HeAr correlation energy prediction analysis for the multipole expansion and the spherical atom model using set1b parameters.
NeAr: Undamped Dispersion Model to CCSD(T)/aug-cc-pV5Z+3s3p2d2f1g
Spherical atom model: $C_6 = 19.0098 + r_s = 1.44115$

Figure e.ib-3c: NeAr correlation energy prediction analysis for the multipole expansion and the spherical atom model using set1b parameters.
HeNe: Undamped Dispersion Model to CCSD(T)/aug-cc-pV5Z+3s3p2d2f1g
Spherical atom model: \( C_6 : 2.89876 + r_s : 1.17130 \)

![Graph showing correlation energy prediction analysis for the multipole expansion and the spherical atom model using set 2a parameters.](image)

Figure e.ib-4a: HeNe correlation energy prediction analysis for the multipole expansion and the spherical atom model using set 2a parameters.
HeAr: Undamped Dispersion Model to CCSD(T)/aug-cc-pV5Z+3s3p2d2f1g
Spherical atom model: $C_6 : 8.82717 + r_s : 1.48485$

Figure e.ib-4b: HeAr correlation energy prediction analysis for the multipole expansion and the spherical atom model using set 2a parameters.
NeAr: Undamped Dispersion Model to CCSD(T)/aug-cc-pV5Z+3s3p2d2f1g
Spherical atom model: $C_6 : 17.98039 + r_s : 1.63055$

Figure e.ib-4c: NeAr correlation energy prediction analysis for the multipole expansion and the spherical atom model using set 2a parameters.
E.ii  “Organic” systems

Although the noble gas systems are ideal to study dispersion, they do not have much chemical applicability. In this section, parameters will be assigned to the carbon and the hydrogen dimers and will be tested for transferability in the H-C dimer.

E.ii.a  H-H, C-C

For the homonuclear dimers, the highest spin cases will be considered. Unlike the noble gases, carbon and hydrogen atoms can form covalent bonds governed by the Pauli Exclusion Principle. Dispersion interaction will not be the main attraction and if the highest spin cases are not considered, the electrons will align with each other to produce diatomic molecules rather than homonuclear dimers. Thus for the carbon dimer, reference calculations will be done for the $^9\Sigma$ state; for the hydrogen dimer, the $^3\Sigma$ state will be considered. Note that the nonet state is not as unrealistic as it may appear: in a single covalent bond, the carbon atom is sp$^3$ hybridized where one of the 2s electron can be thought to be excited to the unoccupied 2p orbital. All the valence electrons will be unpaired and the isolated carbon atom can be represented by the $^5\Sigma$ state. Two of these “hybridized” carbons will make the $^9\Sigma$ state.

The reference correlation curves are calculated using the CCSD(T)/aug-cc-pVQZ method with optimized spdf mid-bond functions. The potential energies and the correlation energies are shown in Figures (e.ia1-1a) to (e.ii-a1-1b). Properties for the interaction are given in Table (e.ia1-1).
Comparison with the noble gas systems show that the magnitude of the hydrogen dimer attraction is about one third of the helium dimer while the equilibrium bond length is about 3 bohrs larger; the carbon dimer shows equilibrium energy to be twice that of He-He.

<table>
<thead>
<tr>
<th>Sys/Prop.</th>
<th>$R_{V=0}$ (bohrs a.u.)</th>
<th>$R_e$ (bohrs a.u.)</th>
<th>$E_e$ (hartrees a.u)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-H</td>
<td>6.80</td>
<td>7.891</td>
<td>-0.000018591</td>
</tr>
<tr>
<td>C-C</td>
<td>7.57</td>
<td>8.522</td>
<td>-0.000074414</td>
</tr>
</tbody>
</table>

TABLE e.iia1-1: Internuclear distances at which the interaction is zero, and at which it is at equilibrium, along with the equilibrium energy for H-H and C-C.

For parameterization, two sets of parameters for hydrogen will be considered. Although the multipole coefficients are not well known for many atoms other than noble gases, they are given for the hydrogen dimer in reference 68. Set 1 will consist of $r_s$ and $r_d$ values that have been nonlinearly least squares fit using the known $C_6$ value; set 2 will consist of all three parameters simultaneously fit to the reference curve. These values are presented in Tables (e.iia1-2a) and (e.iia1-2b). Parameters for C-C are presented in Table (e.iia1-2b).

<table>
<thead>
<tr>
<th>System/Paramter</th>
<th>$C_6$</th>
<th>$r_s$</th>
<th>$r_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-H</td>
<td>6.499027</td>
<td>1.2504±0.0048</td>
<td>1.8522±0.0056</td>
</tr>
</tbody>
</table>

TABLE e.iia1-2a: Hydrogen dimer $r_s$ and $r_d$ values using literature $C_6$ value.

<table>
<thead>
<tr>
<th>System/Paramter</th>
<th>$C_6$</th>
<th>$r_s$</th>
<th>$r_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-H</td>
<td>6.7917±0.0525</td>
<td>1.1255±0.0230</td>
<td>1.7815±0.0132</td>
</tr>
<tr>
<td>C-C</td>
<td>30.244±0.312</td>
<td>1.96511±0.024000</td>
<td>2.3999±0.0153</td>
</tr>
</tbody>
</table>

TABLE e.iia1-2b: Nonlinear least squares fit $C_6$, $r_s$, and $r_d$ for carbon and hydrogen dimer.
Examining the parameters, although the equilibrium energy for hydrogen is less than that of helium, the C₆ coefficient is about the magnitude of the neon dimer value. The carbon dimer C₆ coefficient is in-between that of the neon and the argon dimer. This indicates that carbon and hydrogen more polarizable than the neon atom.

For hydrogen, the spherical atom model can be expanded to predict the higher order multipole coefficients. These values are given in Table (e.ia1-4) and the values from reference 68 are tabulated in Table (e.ia1-3). Note that in Table (e.ia-4), the coefficients are predicted using set 1 and set 2.

<table>
<thead>
<tr>
<th></th>
<th>C₆</th>
<th>C₈</th>
<th>C₁₀</th>
<th>C₁₂</th>
<th>C₁₄</th>
<th>C₁₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.499027</td>
<td>124.39908</td>
<td>3285.82341</td>
<td>1.21486x10⁵</td>
<td>6.06077x10⁶</td>
<td>3.93751x10⁸</td>
</tr>
</tbody>
</table>

TABLE e.ia1-3: Dispersion coefficients for hydrogen dimer.

From the noble gas cases, the spherical atom model overestimated the second-order coefficient while it underestimated the higher terms. For hydrogen, both sets of parameters underestimate all the coefficients.

<table>
<thead>
<tr>
<th></th>
<th>C₆</th>
<th>C₈</th>
<th>C₁₀</th>
<th>C₁₂</th>
<th>C₁₄</th>
<th>C₁₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.7917</td>
<td>103.24065</td>
<td>1046.24097</td>
<td>8.8355x10³</td>
<td>6.71544x10⁴</td>
<td>4.7637x10⁵</td>
</tr>
<tr>
<td>2</td>
<td>6.499027</td>
<td>121.93476</td>
<td>1525.16010</td>
<td>1.58972x10⁴</td>
<td>1.49132x10⁵</td>
<td>1.30574x10⁶</td>
</tr>
</tbody>
</table>

Table e.ia1-4: Predicted multipole coefficients; row 1 is predicted from set 2 and row 2 is from set 1.

Plots similar to the previous section are shown in Figures (e.ia1-2a) to (e.ia1-2b). Since all the multipole coefficients were underestimated, it is not surprising that the spherical atom model converges faster than the London model for both sets. Consistent with majority of the noble gas results, both sets of parameters show that the spherical atom model is comparable with the two and three-termed London
model. Set 2 however shows convergence problem where the asymptotic limit is greater than that of the reference limit.

Both sets of parameters will be evaluated for transferability in the H-C dimer.

**E.ii.b H-C**

The dispersion interaction between the $^5\Sigma$ hydrogen atom and the $^5\Sigma$ carbon will be predicted using the same combination rules as before with the noble gases. Two groups of parameters, set 1a and set 1b, are shown in Table (e.iib-1): set 1a uses set 1 hydrogen parameters and set 1b uses set 2 hydrogen parameters.

<table>
<thead>
<tr>
<th></th>
<th>C$_6$</th>
<th>r$_s$</th>
<th>r$_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC (C$_6$: 6.499027)</td>
<td>14.01986</td>
<td>1.60775</td>
<td>1.98886</td>
</tr>
<tr>
<td>HC (C$_6$: 6.7917)</td>
<td>14.332068</td>
<td>1.5453</td>
<td>2.06771</td>
</tr>
</tbody>
</table>

**TABLE e.iib-1: Predicted coefficients for HC.**

<table>
<thead>
<tr>
<th></th>
<th>C$_6$</th>
<th>r$_s$</th>
<th>r$_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-C</td>
<td>16.078±0.43003</td>
<td>1.2165±0.0763</td>
<td>1.9077±0.0379</td>
</tr>
</tbody>
</table>

**TABLE e.iib-2: Nonlinear least squares fit values for C$_6$, r$_s$, and r$_d$.**

The predicted potential energy curves are shown in Figure (e.iib-1) where set 1a seems to describe too much dispersion energy. Comparing the two sets, Table (e.iib-1) shows that set 1b has a larger dispersion coefficient. Thus, the r$_s$ value for set 1a is too large or the predicted damping radius is too small. For set 1b, the predictions are in good agreement with the reference curve. For set 1a, it is hoped that if literature dispersion coefficient for carbon is used to determine the carbon r$_s$ and r$_d$ values, the parameters would show better transferability. The errors in the well depth predictions are tabulated in Table (e.iib-3).
<table>
<thead>
<tr>
<th></th>
<th>$E_e$ (hartree a.u.)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>-0.000037389</td>
<td></td>
</tr>
<tr>
<td>Set 1a</td>
<td>-0.000041889</td>
<td>2.302%</td>
</tr>
<tr>
<td>Set 1b</td>
<td>-0.00003825</td>
<td>12.036%</td>
</tr>
</tbody>
</table>

TABLE e.iib-3: Set 1a and set 1b error in equilibrium energy predictions.
H-H and C-C interaction energies

Figure e.ia-1a: The reference potential energy curve for H-H and C-C.
Figure e.ii-a-1b: The correlation energy curves for H-H and C-C.
Figure e.ii.a-2a: H-H correlation energy prediction analysis for the multipole expansion and the spherical atom model using parameters from set 1 ($C_6$=literature value; $r_i$ and $r_d$ nonlinear least squares fit).
H-H: Undamped Dispersion Model to CCSD(T)/aug-cc-pVQZ+spdf
Spherical atom model: $C_6 = 6.7917$

Figure e.iiia-2b: H-H correlation energy prediction analysis for the multipole expansion and the spherical atom model using parameters from set 1 ($C_6$, $r_s$ and $r_d$ nonlinear least squares fit).
Figure e.iib-1: Spherical atom model predictions for H-C for set 1a and set 1b.
F Results II: Molecular System H₂-NG

In Section (E), it has been shown that the spherical atom model can successfully describe dispersion forces on spherically symmetric atomic systems. The model will now be tested on simple homonuclear diatomic molecules interacting with noble gases. This provides a simple example of dispersion involving chemical bonds, which is the first step in expanding the theory to practical applications.

The parameters developed in Section (E) and the parameters predicted from the simple geometric combination rule will be called atomic parameters from here on. The transferability of these atomic values to diatomic systems will be tested first and then will be modified to include the changes in the atomic properties of the atoms in molecules.

F i  H-He, H-Ne, H-Ar

Before the spherical atom model is evaluated for H₂-He and H₂-Ne systems, the spherical atom model will first be tested on how well it describes the interaction between a hydrogen atom and the three noble gases. The geometric combination rules for the dispersion coefficient and the damping radius will be used as in the heteronuclear noble gas cases. For simplicity, only one of the possible combinations of parameters will be considered: the parameters predicted from set 1 for the noble gas and set 2 for hydrogen. The predicted values are given below in Table (f.i-1).

The predicted interaction energy curves are shown in Figure (f.i-1). The reference potential energy curve are from CCSD(T) calculations. H, Ne, and Ar are
described with aug-cc-pVTZ basis set while He is described with cc-pVTZ basis set. 

A set of spdf mid bond function was placed in-between the internuclear distance.

<table>
<thead>
<tr>
<th>System/Parameter</th>
<th>C₆</th>
<th>rₛ</th>
<th>rₜₜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-He</td>
<td>3.15001</td>
<td>1.0514</td>
<td>1.55254</td>
</tr>
<tr>
<td>H-Ne</td>
<td>6.53174</td>
<td>1.1683</td>
<td>1.69558</td>
</tr>
<tr>
<td>H-Ar</td>
<td>20.80828</td>
<td>1.30565</td>
<td>1.71672</td>
</tr>
</tbody>
</table>

Table f.i-1: Predicted parameters for H-He, H-Ne, and H-Ar.

The errors for the equilibrium energy predictions are given in Table (f.i-2).

<table>
<thead>
<tr>
<th></th>
<th>Eₑ(CCSD(T))</th>
<th>Eₑ(predicted)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-He</td>
<td>-0.01781746</td>
<td>-0.0233333</td>
<td>30.95%</td>
</tr>
<tr>
<td>H-Ne</td>
<td>-0.04682540</td>
<td>-0.05761905</td>
<td>23.05%</td>
</tr>
<tr>
<td>H-Ar</td>
<td>-0.1423810</td>
<td>-0.1334921</td>
<td>-6.243%</td>
</tr>
</tbody>
</table>

TABLE f.i-2: Set 1a and set 1b error in equilibrium energy predictions. Atomic units are used.

For these cases, the results are not as accurate as with the noble gases where the worst prediction with the noble gases was with the He-Ne system that gave a maximal error of 6.21%. For the current systems, it should be noted that much smaller basis sets and lower level *ab initio* method were used to calculate the reference curves. For H-He, diffuse functions were not added to He and it is predicted that inclusion of these functions to saturate the basis set more will give a lower well depth. For example, calculations from reference 59 estimate the well depth of H-He to be approximately -0.02111 millihartrees. From this result, the error for H-He prediction would be
approximately 10.53%. This discrepancy highlights the importance of including diffuse functions to systems dominated by dispersion interaction.

\textbf{F.ii \ H}_2\text{-He and H}_2\text{-Ne}

The spherical atom model shows that it is able to qualitatively describe the noble gas interaction with hydrogen atom and is able to quantitatively describe the interaction with helium and argon. For the molecular case, additivity of dispersion energy will be assumed: each of the hydrogen atoms in the diatomic molecule will be described by a spherical shell. The noble gas atom, also described by a spherical shell, will interact with each of the shell in the molecule.

Three different “reaction paths” will be considered for \text{H}_2\text{-He} and \text{H}_2\text{-Ne} systems. These approaches are shown in Diagram (f.ii-1) where it can be seen for the linear geometry, all the three nuclei are collinear; the 45 approach will refer to the noble gas approaching at 45° with respect to the center of the hydrogen diatomic bond; the perpendicular approach will refer to the noble gas approaching the molecule such that the noble gas interacts with both hydrogens equally.
For the linear geometry, majority of the correlation energy will arise from the interaction between the noble gas and the nearest hydrogen atom in the diatomic. The distance between the noble gas and the second hydrogen atom will be relatively far such that the correlation contribution will only be small; furthermore, the electrons of this hydrogen will not be as polarizable as the first hydrogen. It can therefore be expected that the total repulsion energy for the linear system will be the least and the equilibrium bond length will be the shortest compared to the other two geometries.

For the perpendicular geometry, although the noble gas interacts equally with both hydrogen atoms (thereby having more correlation energy), the repulsion energy will be the largest because of the number of electrons involved. The equilibrium bond length will be the greatest for this geometry.

- Atomic parameters

Using the atomic parameters for hydrogen and the noble gases from set 2 and set 1 respectively, the predicted parameters for each pair interactions are tabulated in Table (f.ii-1). As mentioned before, the $C_6$ and $r_d$ values arise from the geometric mean. Although the values in Table (f.ii-1) are identical to the ones for H-He, H-Ne, and H-Ar interactions, for the molecular cases, the parameters refer to the interactions between the hydrogen in a molecule with a noble gas atom.

<table>
<thead>
<tr>
<th>System/Paramter</th>
<th>$C_6$</th>
<th>$r_s$</th>
<th>$r_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-He</td>
<td>3.15001</td>
<td>1.0514</td>
<td>1.55254</td>
</tr>
<tr>
<td>H-Ne</td>
<td>6.53174</td>
<td>1.1683</td>
<td>1.69558</td>
</tr>
<tr>
<td>H-Ar</td>
<td>20.80828</td>
<td>1.30565</td>
<td>1.71672</td>
</tr>
</tbody>
</table>
The reference calculations have been calculated with CCSD(T)/aug-cc-pVTZ with spdf mid-bond functions. The bond length of the hydrogen molecule was set to approximately 1.4 bohrs. The predictions for each of the three geometries of each system are shown in Figures (f.ii-2a) to (f.ii-2b). The errors for the energy predictions are given in Tables (f.ii-2a) to (f.ii-2b).

<table>
<thead>
<tr>
<th>H₂-He</th>
<th>Eₑ(CCSD(T))</th>
<th>Eₑ(predicted)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>-0.0457143</td>
<td>-0.1143254</td>
<td>-150.09%</td>
</tr>
<tr>
<td>45</td>
<td>-0.0405556</td>
<td>-0.1032341</td>
<td>-154.55%</td>
</tr>
<tr>
<td>90</td>
<td>-0.0426191</td>
<td>-0.0926587</td>
<td>-117.41%</td>
</tr>
</tbody>
</table>

Table (f.ii-2a): Errors in the well depth predictions using atomic parameters for H₂-He.

<table>
<thead>
<tr>
<th>H₂-Ne</th>
<th>Eₑ(CCSD(T))</th>
<th>Eₑ(predicted)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>-0.1019048</td>
<td>-0.2262698</td>
<td>-122.04%</td>
</tr>
<tr>
<td>45</td>
<td>-0.0959524</td>
<td>-0.2159524</td>
<td>-125.06%</td>
</tr>
<tr>
<td>90</td>
<td>-0.0930952</td>
<td>-0.2051190</td>
<td>120.33%</td>
</tr>
</tbody>
</table>

Table (f.ii-2b): Errors in the well depth predictions using atomic parameters for H₂-Ne.

For both systems, it is evident that the spherical atom model fails to predict the dispersion energy at all three geometries with atomic parameters.

- **Modified molecular C₆ parameter**

In molecular cases, because the dispersion interaction is no longer spherically symmetric, the spherical atom model will need modifications. For example, although
H₂ may seem to have an isotropic electron density, the dispersion interaction will highly depend on the angular configuration of the system. That is, a hydrogen atom will be equally polarizable at all angles; however, in a molecule, the polarizability tensor components will not be uniform. The polarizability tensor components of hydrogen atom and hydrogen in H₂ have been calculated with MP2/aug-cc-pVTZ and are tabulated in Table (f.ii-3).

<table>
<thead>
<tr>
<th></th>
<th>α_{xx}</th>
<th>α_{yy}</th>
<th>α_{zz}</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_{molec}</td>
<td>4.608</td>
<td>4.608</td>
<td>6.424</td>
</tr>
<tr>
<td>H_{atom}</td>
<td>4.476</td>
<td>4.476</td>
<td>4.476</td>
</tr>
</tbody>
</table>

Table f.ii-3: Polarizability of H in H₂ and of a hydrogen atom.

From Table (f.ii-3), it can be seen that for H in H₂ (H_{molec}), the electron density is more polarizable along the direction of the bond but is equally polarizable else wise. In order to take this anisotropy into account, the dispersion coefficient will be modified such that it takes into account the average interaction of the noble gas atom interacting with H_{molec} overall orientation. The new C₆ will be calculated from:

\[ C_{6,\text{molec}} = C_{6,\text{atom}} \frac{\alpha_{xx}^{\text{A}_{2}} + \alpha_{yy}^{\text{A}_{2}} + \alpha_{zz}^{\text{A}_{2}}}{\alpha_{\text{AA}}^{\text{A}} + \alpha_{\text{BB}}^{\text{A}}} \sqrt{\frac{C_{6}^{\text{AA}} + C_{6}^{\text{BB}}}{C_{6}^{\text{AA}} + C_{6}^{\text{BB}}}}. \]

and will be called the molecular dispersion coefficient. For H₂-He system, this value calculates to be 1.83445 in atomic units.

The spherical atom model predictions using this modification with atomic spherical radius and atomic damping radius are shown in Figure (f.ii-2). The errors for the predictions are given in Table (f.ii-4)

It is seen that the error in the well depth prediction is drastically reduced from
the previous case. The success of this modification should also be tested on H2-Ne and H2-Ar systems.

<table>
<thead>
<tr>
<th></th>
<th>$E_0$(CCSD(T))</th>
<th>$E_0$(predicted)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>-0.0405555</td>
<td>-0.0457143</td>
<td>11.28%</td>
</tr>
<tr>
<td>45</td>
<td>-0.0369444</td>
<td>-0.0405556</td>
<td>7.93%</td>
</tr>
<tr>
<td>90</td>
<td>-0.0338492</td>
<td>-0.0426191</td>
<td>20.58%</td>
</tr>
</tbody>
</table>

Table f.ii-4: Errors in equilibrium energy predictions using molecular C$_6$ coefficient for H$_2$-He.

- **Molecular parameters**

When an atom forms a bond, it is generally known that the atomic electron density changes. For hydrogen, when it forms H$_2$, the electron density contracts. Thus, the “size” of the atom in the molecule changes, indicating that the spherical atom radius and the damping radius should be modified. Currently, there is no obvious method to obtain these molecular radial values. Instead, all three parameters – C$_6$, $r_s$, and $r_d$ – can be optimized for each atom in a molecule and the transferability of these values can be tested. This method may be the best method to parameterize molecular systems since there are no clear guidelines as to how to assign “atomic” properties to atoms in molecules.

For H$_{molec}$ parameters, the spherical atom parameters along with the damping radius have been simultaneously optimized to all three geometries for the H$_2$-He system until the lowest rms error was obtained. These parameters represent the H$_2$-He system and in order to decouple of the helium parameters from the H$_{molec}$ parameters, the geometric combination rule is algebraically manipulated to obtain:
\[ C_6^{H_{\text{molec}}} = \left[ C_6^{H_2-\text{He}} \right]^2 / C_6^{\text{He}-\text{He}} \]

and

\[ r_d^{H_{\text{molec}} - H_{\text{molec}}} = \left[ r_d^{H_2-\text{He}} \right]^2 / r_d^{\text{He}-\text{He}}. \]

The optimized parameters are given in Table (f.ii-5) along with predicted parameters for H2-Ne.

<table>
<thead>
<tr>
<th>System/Parameter</th>
<th>C_6</th>
<th>r_s</th>
<th>r_d</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(2)</td>
<td>2.47953</td>
<td>1.94946</td>
<td>1.64585</td>
</tr>
<tr>
<td>H2-He</td>
<td>1.90330</td>
<td>1.46338</td>
<td>1.49226</td>
</tr>
<tr>
<td>H2-Ne</td>
<td>3.94661</td>
<td>1.58028</td>
<td>1.62975</td>
</tr>
</tbody>
</table>

Table f.ii-5: Optimized parameters for H in H_2 is given in the first row; the spherical atom molecular parameters for H2-He and H2-Ne are tabulated following.

From Table (f.ii-5), it is observed that the dispersion coefficient is smaller in magnitude than the atomic dispersion coefficient. It may be noted that the molecular C_6 value calculated previously also decreased in magnitude, indicating that H_{molec} is less polarizable than a hydrogen atom. The spherical radius is about 0.4 bohrs larger in molecules.

The predictions with these parameters for the helium and the neon interaction with H_2 are shown in Figures (f.ii-3) and (f.ii-4). The errors in the well depth predictions are given in Tables (f.ii-6) and (f.ii-7).

<table>
<thead>
<tr>
<th>H2-He</th>
<th>E_e(CCSD(T))</th>
<th>E_e(predicted)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>-0.0405555</td>
<td>-0.04738095</td>
<td>16.83%</td>
</tr>
<tr>
<td>45</td>
<td>-0.0369444</td>
<td>-0.04369048</td>
<td>18.26%</td>
</tr>
</tbody>
</table>
Table f.ii-6: Error in equilibrium energy predictions using molecular parameters for H$_2$-He.

<table>
<thead>
<tr>
<th>H$_2$-He</th>
<th>$E_e$(CCSD(T))</th>
<th>$E_e$(predicted)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>-0.1019048</td>
<td>-0.1028571</td>
<td>0.934%</td>
</tr>
<tr>
<td>45</td>
<td>-0.0959524</td>
<td>-0.09785714</td>
<td>1.99%</td>
</tr>
<tr>
<td>90</td>
<td>-0.0930952</td>
<td>-0.09428571</td>
<td>1.27%</td>
</tr>
</tbody>
</table>

Table f.ii-7: Error in equilibrium energy predictions using molecular parameters for H$_2$-Ne.

Although the parameters were fit for H$_2$-He, the predictions for the H$_2$-Ne are significantly better. The spherical atom model should also be tested for the H$_2$-Ar system to measure the physical significance of the optimized molecular parameters.

These three methods of parameterization will next be applied to $F_{molec}$ in F$_2$. 
H-He, H-Ne, H-Ar interaction energies

\[ C_6^{\text{HNG}} = (C_6^{\text{H-H}} C_6^{\text{H-NG}})^{1/2} \]

\[ r_s^{\text{HNG}} = (r_s^{\text{H-H}} + r_s^{\text{H-NG}})/2 \]

\[ r_d^{\text{HNG}} = (r_d^{\text{H-H}} - r_d^{\text{H-NG}})/2 \]

<table>
<thead>
<tr>
<th>Interaction Energy</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-He E(CCSD(T)/3-Zeta+spdf)</td>
<td></td>
</tr>
<tr>
<td>HHe SAM*Damping+HF/3-Zeta+spdf</td>
<td></td>
</tr>
<tr>
<td>HNe E(CCSD(T)/3-Zeta+spdf)</td>
<td></td>
</tr>
<tr>
<td>HNe SAM*Damping+HF/3-Zeta+spdf</td>
<td></td>
</tr>
<tr>
<td>HAr E(CCSD(T)/3-Zeta+spdf)</td>
<td></td>
</tr>
<tr>
<td>HAr SAM*Damping+HF/3-Zeta+spdf</td>
<td></td>
</tr>
</tbody>
</table>

Figure f.i-1: Interaction energy curve predictions for H-He, H-Ne, and H-Ar.
H$_2$-He Interaction energies from atomic parameters

\[
\begin{align*}
C_6^{\text{HNG}} &= \left( C_6^{\text{H-H}} C_6^{\text{NGNG}} \right)^{1/2} \\
r_s^{\text{HNG}} &= \left( r_s^{\text{H-H}} + r_s^{\text{NGNG}} \right)/2 \\
r_d^{\text{HNG}} &= \left( r_d^{\text{H-H}} + r_d^{\text{NGNG}} \right)
\end{align*}
\]

Linear E(CCSD(T)/aug-cc-pVTZ+spdf)
Linear SAM*Damping+HF/aug-cc-pVTZ+spdf
45 E(CCSD(T)/aug-cc-pVTZ+spdf)
45 SAM*Damping+HF/aug-cc-pVTZ+spdf
90 E(CCSD(T)/aug-cc-pVTZ+spdf)
90 SAM*Damping+HF/aug-cc-pVTZ+spdf

Figure f.ii-1a: Predicted potential energy curves for all three geometries for H$_2$-He using atomic parameters.
**H$_2$-Ne Interaction energies from atomic parameters**

\[
C_6^{\text{HNG}} = (C_6^{\text{H-H}} C_6^{\text{NGNG}})^{1/2} \quad r_s^{\text{HNG}} = (r_s^{\text{H-H}} + r_s^{\text{NGNG}})/2 \quad r_d^{\text{HNG}} = (r_d^{\text{H-H}} r_d^{\text{NGNG}})
\]

**Linear E(CCSD(T)/aug-cc-pVTZ+spdf)**

**Linear SAM*Damping+HF/aug-cc-pVTZ+spdf**

**45 E(CCSD(T)/aug-cc-pVTZ+spdf)**

**45 SAM*Damping+HF/aug-cc-pVTZ**

**90 E(CCSD(T)/aug-cc-pVTZ+spdf)**

**90 SAM*Damping+HF/aug-cc-pVTZ+spdf**

---

**Figure f.ii-1b:** Predicted potential energy curves for all three geometries for H$_2$-Ne using atomic parameters.
H$_2$-He Interaction energies from molecular C$_6$ parameter

Figure f.ii-2: Predicted potential energy curves for H$_2$-He using modified atomic C$_6$ coefficient. The new coefficient will be called molecular C$_6$ coefficient.
Figure f.ii-3: Predicted potential energy curves for H₂-He using molecular parameters.
Figure f.ii-4: Predicted potential energy curves for H₂-Ne using molecular parameters.
G Results II: Molecular System F₂-NG

For F_{molec}, the three geometries for F₂-He system will be tested to measure the shortcomings of applying atomic parameters to molecular systems and the success of only modifying the dispersion coefficient. Because of the electron density distribution of the fluorine molecule, this system will also indicate if it is possible to assign a single set of parameters to describe different orientations.

For F₂, because the higher angular orbitals are occupied compared to H₂, the dispersion interaction with noble gas atoms will be highly anisotropic. In the perpendicular geometry, as the noble gas approach F₂, electronic repulsion will rise rapidly because of the occupied π orbitals. This will make the equilibrium bond length much longer than the linear geometry. A diagram of the three approaches is given below. Before parameters are evaluated, the atomic parameters for F₂ ³Π will be developed first.

G.i F-F

For F₂, ³Π state is considered to avoid formation of a sigma bond. Because
the literature \( C_6 \) coefficient is currently unknown, all three parameters were nonlinear least square fit. The reference curve was calculated with CCSD(T)/aug-cc-pVTZ with spdf mid-bond functions. The parameters are given in Table (g.i-1).

<table>
<thead>
<tr>
<th>System/Parameter</th>
<th>( C_6 )</th>
<th>( r_s )</th>
<th>( r_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-F</td>
<td>8.0557</td>
<td>1.2600</td>
<td>1.7412</td>
</tr>
</tbody>
</table>

Table g.i-1: Nonlinear least squares fit parameters for F-F.

Similar with the hydrogen case, the atomic parameters should be tested for the dispersion interaction between fluorine atom and the three noble gases. Careful considerations should be taken into account so that the orientation of the fluorine atom is fixed with respect to the noble gas in order to avoid curve crossing. Also, if the singly occupied orbital is along the internuclear distance, the noble gas valence electron may delocalize unto the fluorine atom. The total intermolecular correlation energy of the system would not purely consist of dispersion energy.

\textit{G.ii F}_2\textit{-He}

- \textit{Atomic Parameters}

  The geometric mean of the fluorine atomic parameters and the noble gas atomic parameters are used for predictions. These parameters will be tested for the three orientations of both helium and neon systems. The predicted parameters are given in Table (g.i-2).
The predicted potential energy curves are shown in Figures (g.i-1) and (g.i-2) and the error in the equilibrium energy prediction is tabulated in Tables (f.ii-4a) to (f.ii-4b).

It is observed that the atomic parameters predict the potential well depth better than the systems with H₂. However, the results are not consistent; this indicates that the physicality of the problem is not correctly addressed.

- Modified molecular $C_6$ parameter

The polarizability tensors for both fluorine atom and $F_{molec}$ are shown in Table (f.ii-5).
Comparing the values with hydrogen, it is observed that the polarizability almost quadruples along the fluorine bond axis while for hydrogen, the value increases approximately by a factor of 1.5. Comparing the other components, the polarizability tensor almost doubles, indicating that the interaction is highly anisotropic.

The molecular $C_6$ coefficient calculates to be 3.91391 (in atomic units) and the potential energy curve predictions for F$_2$-He are shown in Figure (g.i-3). The errors are given in Table (f.ii-6)

<table>
<thead>
<tr>
<th>F$_2$-He</th>
<th>$E_e$(CCSD(T))</th>
<th>$E_e$(predicted)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>-0.1545833</td>
<td>-0.132500</td>
<td>-14.29%</td>
</tr>
<tr>
<td>45</td>
<td>-0.0970833</td>
<td>-0.097916</td>
<td>0.8578%</td>
</tr>
<tr>
<td>90</td>
<td>-0.1404167</td>
<td>-0.178333</td>
<td>27.00%</td>
</tr>
</tbody>
</table>

Table f.ii-4: Error in equilibrium energy predictions using molecular $C_6$ for F$_2$-He.

For this set of parameters, the error for linear and 45 geometry decreased but the error for the perpendicular geometry increased. Since the atomic parameters fortuitously gave accurate predictions for the perpendicular approach, it is concluded that using the molecular $C_6$ value significantly improves the spherical atom model predictions.

Table f.ii-5: The polarizability of F$_2$ and F atom.
- Molecular parameters

A new set of molecular parameters are generated by optimizing all three parameters such that the rms error to the fit of all three geometries of the F$_2$-He system is minimum. The parameters for fluorine in a molecule are given in Table (f.ii-7) along with the predicted molecular parameters for F$_2$-He and F$_2$-Ne.

<table>
<thead>
<tr>
<th>System/Parameters</th>
<th>C$_6$</th>
<th>r$_s$</th>
<th>r$_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$_{molec}$</td>
<td>15.44</td>
<td>0.46298</td>
<td>0.7982</td>
</tr>
<tr>
<td>F$_2$-He</td>
<td>4.7496</td>
<td>0.72014</td>
<td>1.03923</td>
</tr>
<tr>
<td>F$_2$-Ne</td>
<td>9.84835</td>
<td>0.83704</td>
<td>1.13496</td>
</tr>
</tbody>
</table>

Table f.ii-7: Molecular parameters for F$_{molec}$ and predicted molecular parameters for F$_2$-He and F$_2$-Ne.

The predicted potential energy curves are shown in Figures (g.i-4) to (g.i-5). From observing the numerical values of the radii, it is evident that these values may be an unrealistic description of the “atoms” due to their small magnitude. Simultaneous fit to all three geometries may not always produce reliable results and inclusion of angular dependence may be necessary.
$C_6^{\text{FNG}} = (C_6^{\text{F-F}} C_6^{\text{NGNG}})^{1/2}$

$r_s^{\text{FNG}} = (r_s^{\text{F-F}} + r_s^{\text{NGNG}})/2$

$r_d^{\text{FNG}} = (r_d^{\text{F-F}} r_d^{\text{NGNG}})$

Figure (g.i-1): Potential energy predictions for F$_2$-He using atomic parameters.
Figure (g.i-2): Potential energy predictions for F₂-Ne using atomic parameters.
Figure g.i-3: Predicted potential energy curves for F₂-He using modified atomic C₆ coefficient. The new coefficient will be called molecular C₆ coefficient.
Figure f.ii-3: Predicted potential energy curves for H$_2$-He using molecular parameters.
Conclusion

Because many terms in the multipole expansion are needed to describe dispersion accurately (where the damping function will correct its short range behavior), the London model is not readily applicable. The higher order multipole coefficients require significant amount of time to calculate (although not mentioned here) and it will be difficult to decouple the several dispersion coefficients to find its nonlinear least squares fit value if the fitted parameters are wanted to be used. For atomic systems, the spherical atom model shows that it effectively takes into account higher order multiple terms and the parameters can be easily obtained by fitting the spherical atom radius value to the known $C_6$ coefficient or by nonlinear least squares fitting both parameters (along with the damping function parameter). Furthermore, because there are much fewer parameters to obtain than the London model, there has currently been no case where unreasonable values were obtained. The spherical atom model thus shows great potential to be a more convenient model to use than the London model for atomic systems.

However, for the molecular systems a general method to obtain parameters has not been ascertained yet. It is clear that the atomic parameters are not transferable to the molecular systems: these parameters fail to consistently give accurate predictions for the well depth and the equilibrium bond length. Although modifying the atomic dispersion coefficient in terms of polarizability seems promising, this method needs to be tested for more systems.

Reassigning each “molecular atoms” to new molecular parameters intuitively
appears to be the correct method to physically describe the changes in the atoms in molecules. However, it appears that directionality of the interactions needs to be taken into account to describe the anisotropy of the interaction surface. Although it was not mentioned here, an attempt to describe angular dependence to the damping radius has been tested. For the three geometries, it has been mentioned before that the repulsion energy increases from the linear to the perpendicular geometry. The shift in the exponential repulsion curve from the linear to the perpendicular geometry was first calculated and the damping radius was adjusted according to the shift. However, it was realized that the damping radius was only related to the distance at which dispersion energy is zero and not the repulsion between the electrons.

A hopeful method that should be tested more extensively for all methods is to consider the simultaneous alignment of instantaneous dipoles induced by the noble gas. Considering the perpendicular geometry, from the diagram shown on the side, the non-perpendicular components of the dipole moments arising from two nuclear centers cancel. The spherical atom does not take these cancellations into account and the dispersion energy is overestimated. Projecting the induced dipole moments onto the perpendicular axes should be taken into account. It is not expected however that this will give perfect results since pair-wise additivity was assumed to calculate dispersion.
To compare the two dispersion models for molecular systems, 2-dimensional potential energy plots for H$_2$-He and F$_2$-He are shown in Figures (H.i-1a-c) and (H.i-2a-c). The reference curves have been obtained from interpolation of CCSD(T)/aug-cc-pVTZ curves. The key features of these curves are the local minima at the linear and perpendicular geometry. For the surface predicted by the multipole expansion, the parameters have been optimized to the linear, 45, and perpendicular geometry. No damping function has been used. The spherical atom model surfaces have been calculated with the molecular parameters with the spherical atom model damping function. Comparison of the predicted surfaces of both models shows that both are capable of predicting the two local minima. However, this distinction may be attributed to the SCF component of the interaction energy.

If the London model is damped, it is predicted that more terms are needed to get predictions as accurate as the spherical atom model.
Figure h.i-1a: Reference potential energy surface for H$_2$-He.
Figure h.i-1b: Spherical atom model potential energy surface prediction for H₂-He.
H2-He Two-term Multipole Expansion Potential Energy Surface (mEh)

Figure h.i-1c: London model potential energy surface prediction for H2-He.
Figure h.i-2a: Reference potential energy surface for F₂-He.
Figure h.i-2b: Spherical atom model potential energy surface prediction for $F_2$-He.
Figure h.i-2c: London model potential energy surface prediction for F₂-He.
Appendix

I.i Proof of the Variational Theorem

The variation theorem states that any wavefunction that is not the eigenfunction to the Hamiltonian will give a higher energy than the true energy eigenvalue. Mathematically, this can be expressed as:

$$\int \phi^* H \phi \, d\tau \geq E_i$$  \hspace{1cm} (g.i-1)

The proof is given below.

For any trial normalized wavefunction $\phi$, it can be described by a complete set of orthogonal eigenfunctions to give

$$\phi(R) = \sum_k a_k \psi_k$$ \hspace{1cm} (g.i-2)

where

$$\sum_k |a_k|^2 = 1.$$ \hspace{1cm} (g.i-3)

From (g.i-2), the energy can be calculated to be:

$$E = \int \phi^* \hat{H} \phi \, d\tau = \sum_k a_k^* \psi_k^* \hat{H} \sum_j a_j \psi_j \, d\tau$$ \hspace{1cm} (g.i-4a)

$$= \int \sum_k a_k^* \psi_k^* \sum_j a_j \hat{H} \psi_j \, d\tau = \int \sum_k a_k^* \psi_k^* \sum_j a_j E_j \psi_j \, d\tau$$ \hspace{1cm} (g.i-4b)

Because $k$ and $j$ are independent of each other, equation (g.i-4b) can be rewritten as:

$$\int \sum_k \sum_j a_k^* a_j E_j \psi_k^* \psi_j \, d\tau = \sum_k \sum_j a_k^* a_j \int \psi_k^* \psi_j \, d\tau.$$ \hspace{1cm} (g.i-5)

Since the $\psi$’s are orthogonal, (g.i-5) simplifies to:
\[ = \sum_{k} a^*_k a_k E_k = \sum_{k} |a_k|^2 E_k. \quad (g.i-6) \]

For ground state energy represented as \( E_{k=1} \), it is true that:

\[ E_k \geq E_1 \quad (g.i-7) \]

where the equality holds if \( k=1 \). So then:

\[ |a_k|^2 E_k \geq |a_1|^2 E_1 \quad (g.i-8) \]

Putting all the relationships together, it can be shown that:

\[ \int \phi^* \hat{H} \phi \, dt = \sum_{k} |a_k|^2 E_k \geq \sum_{k} |a_k|^2 E_1 = E_1. \quad (g.i-9) \]

Therefore, any trial wavefunctions that are not the true solutions to the ground state Hamiltonian give upperbound energies.

The proof does not change if \( \phi \) is not normalized since a constant can be multiplied to \( \phi \) for normalization. The variation theorem for this case can be written as:

\[ N \int \phi^* \hat{H} \phi \, dt = \frac{\int \phi^* \hat{H} \phi \, dt}{\int \phi^* \phi \, dt} \geq E_1. \quad (g.i-10) \]

where \( N \) is the normalization constant.

**I.ii Nondegenerate Perturbation Theory**

The perturbation theory breaks up the Hamiltonian into:

\[ \hat{H} = \hat{H}^{(0)} + \hat{H}^{(i)} + \ldots. \quad (g.ii-1) \]

where \( \hat{H} \) is the full Hamiltonian and \( \hat{H}^{(i)} \) is the “unperturbed” or the zeroth order Hamiltonian:

\[ \hat{H}^{(0)} \psi^{(0)} = E^{(0)} \psi^{(0)}, \quad (g.ii-2) \]

Introducing a perturbation parameter \( \lambda \), (g.ii-1) can be rewritten as
\[ \hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)}. \]  
(g.ii-3)

Corresponding to (g.ii-3), the wavefunction $\psi$ can be approximated by taking the Taylor series expansion:

\[ \psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \lambda^3 \psi_n^{(3)} + \ldots. \]  
(g.ii-4)

The energy $E$ can be also expanded to give

\[ E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + \ldots \]  
(g.ii-5)

Using (g.ii-3), (g.ii-4), and (g.ii-5), the Schrödinger equation can be written as:

\[ (\hat{H}^{(0)} + \lambda \hat{H}^{(1)}) (\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \ldots) = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + \ldots) (\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \ldots) \]  
(g.ii-6)

If all the terms with like powers of $\lambda$ are collected then (g.ii-6a) can be rewritten as

\[ \lambda = 0 \quad H^{(0)} \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)} \]  
(g.ii-7a)

\[ \lambda^1 : \quad H^{(0)} \psi_n^{(1)} + H^{(1)} \psi_n^{(0)} = E_n^{(0)} \psi_n^{(1)} + E_n^{(1)} \psi_n^{(0)} \]  
(g.ii-7b)

\[ \lambda^2 : \quad H^{(0)} \psi_n^{(2)} + H^{(1)} \psi_n^{(1)} = E_n^{(0)} \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^{(0)} \]  
(g.ii-7c)

\[ \lambda^3 : \quad H^{(0)} \psi_n^{(3)} + H^{(1)} \psi_n^{(2)} = E_n^{(0)} \psi_n^{(3)} + E_n^{(1)} \psi_n^{(2)} + E_n^{(2)} \psi_n^{(1)} + E_n^{(3)} \psi_n^{(0)} \]  
(g.ii-7d)

\[ \ldots \]

Equating all the like powers of $\lambda$ on both sides of the equation now gives

\[ \lambda = 0 \quad H^{(0)} \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)} \]

\[ \lambda^1 : \quad H^{(0)} \psi_n^{(1)} + H^{(1)} \psi_n^{(0)} = E_n^{(0)} \psi_n^{(1)} + E_n^{(1)} \psi_n^{(0)} \]

\[ \lambda^2 : \quad H^{(0)} \psi_n^{(2)} + H^{(1)} \psi_n^{(1)} = E_n^{(0)} \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^{(0)} \]

\[ \lambda^3 : \quad H^{(0)} \psi_n^{(3)} + H^{(1)} \psi_n^{(2)} = E_n^{(0)} \psi_n^{(3)} + E_n^{(1)} \psi_n^{(2)} + E_n^{(2)} \psi_n^{(1)} + E_n^{(3)} \psi_n^{(0)} \]

\[ \ldots \]

The solutions from the first power of $\lambda$ will be called first order perturbation; solutions from the second power of $\lambda$ will be called second order perturbation, etc.

Writing in terms of Dirac notation, the inner product with $\langle \psi_n^{(0)} \rangle$ and (g.ii-8b) gives:

\[ \langle \psi_n^{(0)} | H^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle = E_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + E_n^{(1)} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle . \]  
(g.ii-9a)
Since $\hat{H}$ is a Hermitian operator,

$$\langle \psi_n^{(0)} | H^{(0)} | \psi_n^{(0)} \rangle = \langle H^{(0)} | \psi_n^{(0)} \rangle | \psi_n^{(0)} \rangle = E_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle.$$  \hspace{1cm} \text{(g.ii-9b)}

and (g.ii-9a) will simplify to:

$$E_n^{(i)} = \langle \psi_n^{(0)} | H^{(i)} | \psi_n^{(0)} \rangle.$$  \hspace{1cm} \text{(g.ii-10)}

(g.ii-10) is the first order perturbation energy that can be solved since the unperturbed wavefunction is known and the perturbation Hamiltonian is assigned.

To solve for the first order wavefunction, (g.ii-8b) can be rewritten as

$$\langle \psi_n^{(0)} | (H^{(0)} - E_n^{(0)}) | \psi_n^{(0)} \rangle = -\langle (H^{(0)} - E_n^{(0)}) | \psi_n^{(0)} \rangle,$$  \hspace{1cm} \text{(g.ii-11a)}

$$= (H^{(0)} - E_n^{(0)}) \psi_n^{(i)} = (H^{(0)} - E_n^{(0)}) \psi_n^{(0)}$$  \hspace{1cm} \text{(g.ii-11b)}

where all the terms on the right side are known values. Since the unperturbed wavefunction forms a complete set, $\psi_n^{(i)}$ can be written as

$$\psi_n^{(i)} = \sum_{m=n} \psi_m^{(0)}$$  \hspace{1cm} \text{(g.ii-12)}

Substituting this relationship into (g.ii-11b) will give:

$$\sum_{m=n} (H^{(0)} \psi_m^{(0)} - E_n^{(0)} \psi_m^{(0)} = - (H^{(0)} - E_n^{(0)}) \psi_n^{(0)}$$  \hspace{1cm} \text{(g.ii-13)}

Taking the inner product with $\langle \psi_k^{(0)} |$ and (g.ii-13) will give:

$$\sum_{m=n} \langle \psi_k^{(0)} | H^{(0)} | \psi_m^{(0)} \rangle + E_n^{(0)} \langle \psi_k^{(0)} | \psi_m^{(0)} \rangle = -\langle \psi_k^{(0)} | \psi_n^{(0)} \rangle + E_n^{(0)} \langle \psi_k^{(0)} | \psi_n^{(0)} \rangle$$  \hspace{1cm} \text{(g.ii-14a)}

(g.ii-14a) can be simplified to:

$$\sum_{m=n} (E_m^{(0)} - E_n^{(0)}) \langle \psi_k^{(0)} | \psi_m^{(0)} \rangle = -\langle \psi_k^{(0)} | \psi_n^{(0)} \rangle - E_n^{(0)} \langle \psi_k^{(0)} | \psi_n^{(0)} \rangle$$  \hspace{1cm} \text{(g.ii-14b)}

Using the orthogonality relationship, the summation on the left side of (g.ii-14b) reduces to one term and the last term on the right side cancels since $n \neq k$. So then, (g.ii-14b) becomes
\[ (E_k^{(0)} - E_n^{(0)}) c_k^{(n)} = - \langle \psi_k^{(0)} | \hat{H}^{(1)} | \psi_n^{(0)} \rangle \]  
\hspace{1cm} \text{(g.ii-15)}

to give
\[ c_k^{(n)} = \frac{\langle \psi_k^{(0)} | \hat{H}^{(1)} | \psi_n^{(0)} \rangle}{E_k^{(0)} - E_n^{(0)}} \]  
\hspace{1cm} \text{(g.ii-16)}

Substituting (g.ii-16) into the linear expansion of \( \psi_n^{(1)} \) gives:
\[ \psi_n^{(1)} = \sum_{m=n} \frac{\langle \psi_m^{(0)} | \hat{H}^{(1)} | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})} \psi_m^{(0)} \]  
\hspace{1cm} \text{(g.ii-17)}

For the second order energy, taking the inner product with \( < \psi_n^{(0)} | \) and (g.ii-8c) will give:
\[ \langle \psi_n^{(0)} | H^{(0)} | \psi_n^{(2)} \rangle + \langle \psi_n^{(0)} | H^{(0)} | \psi_n^{(1)} \rangle = E_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle + E_n^{(1)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + E_n^{(2)} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle \]  
\hspace{1cm} \text{(g.ii-18a)}
\[ = \langle \psi_n^{(2)} | H^{(0)} | \psi_n^{(0)} \rangle + \langle \psi_n^{(1)} | H^{(1)} | \psi_n^{(0)} \rangle = E_n^{(0)} \langle \psi_n^{(2)} | \psi_n^{(0)} \rangle + E_n^{(1)} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle + E_n^{(2)} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle \]  
\hspace{1cm} \text{(g.ii-18b)}
\[ = E_n^{(0)} \langle \psi_n^{(2)} | \psi_n^{(0)} \rangle + \langle \psi_n^{(0)} | \hat{H}^{(1)} | \psi_n^{(1)} \rangle = E_n^{(0)} \langle \psi_n^{(2)} | \psi_n^{(0)} \rangle + E_n^{(1)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + E_n^{(2)} \rangle \]  
\hspace{1cm} \text{(g.ii-18c)}

Using the definition of \( \psi_n^{(1)} \) from (g.ii-12), (g.ii-18c) can be rewritten as
\[ E_n^{(2)} = \langle \psi_n^{(0)} | \hat{H}^{(1)} | \psi_n^{(1)} \rangle \]  
\hspace{1cm} \text{(g.ii-19a)}
\[ = \sum_{m=n} c_m^{(n)} \langle \psi_n^{(0)} | H^{(0)} | \psi_m^{(0)} \rangle \]  
\hspace{1cm} \text{(g.ii-19b)}

Substituting (g.ii-16) into (g.ii-19b) will give
\[ E_n^{(2)} = \sum_{m=n} \frac{| \langle \psi_m^{(0)} | \hat{H}^{(1)} | \psi_n^{(0)} \rangle |^2}{E_n^{(0)} - E_m^{(0)}} \]  
\hspace{1cm} \text{(g.ii-20)}

For the third order perturbation energy, rewriting (g.ii-8d) gives:
\[ (H^{(1)} - E_n^{(1)}) \psi_n^{(2)} - E_n^{(3)} \psi_n^{(0)} - E_n^{(2)} \psi_n^{(1)} = (E_n^{(0)} - H^{(0)}) \psi_n^{(3)} \]  
\hspace{1cm} \text{(g.ii-21)}

Taking the inner product with \( < \psi_k^{(0)} | \) and (g.ii-21) will give
\[
\langle \psi^{(0)}_n | H^{(0)} | \psi^{(2)}_n \rangle - E^{(1)} - E^{(2)} \langle \psi^{(0)}_n | \psi^{(3)}_n \rangle - E^{(2)} \langle \psi^{(0)}_n | \psi^{(1)}_n \rangle = E^{(1)} \langle \psi^{(0)}_n | \psi^{(1)}_n \rangle - \langle \psi^{(0)}_n | H^{(0)} | \psi^{(2)}_n \rangle. \quad (\text{g.ii-22})
\]

Using orthogonality relationship will simplify (g.ii-22) to:

\[
\langle \psi^{(0)}_n | \hat{H}^{(0)} | \psi^{(2)}_n \rangle - E^{(1)} \langle \psi^{(0)}_n | \psi^{(3)}_n \rangle - E^{(2)} \langle \psi^{(0)}_n | \psi^{(1)}_n \rangle = E^{(1)} \langle \psi^{(0)}_n | \psi^{(2)}_n \rangle - E^{(1)} \langle \psi^{(0)}_n | \psi^{(0)}_n \rangle = 0 \quad (\text{g.ii-23})
\]

Using the definition of \( \psi^{(1)}_n \) from (g.ii-12)

\[
E^{(3)}_n = \langle \psi^{(0)}_n | \hat{H}^{(1)} | \psi^{(2)}_n \rangle - E^{(1)} \langle \psi^{(0)}_n | \psi^{(3)}_n \rangle = \langle \psi^{(2)}_n | \hat{H}^{(1)} - E^{(1)} | \psi^{(0)}_n \rangle \quad (\text{g.ii-24})
\]

Using relationship from (g.ii-11b), (g.ii-24) can be rewritten as

\[
E^{(3)}_n = \langle \psi^{(2)}_n | H^{(0)} - E^{(1)} | \psi^{(0)}_n \rangle = \langle \psi^{(1)}_n | H^{(0)} - E^{(0)} | \psi^{(2)}_n \rangle. \quad (\text{g.ii-25})
\]

Then using the relationship from (g.ii-8c)

\[
H^{(0)} \psi^{(2)}_n - E^{(1)} \psi^{(1)}_n = E^{(1)} \psi^{(2)}_n + E^{(2)} \psi^{(0)}_n - H^{(1)} \psi^{(1)}_n \quad (\text{g.ii-26})
\]

(g.ii-25) can be rewritten then as

\[
E^{(3)}_n = \langle \psi^{(1)}_n | \hat{H}^{(1)} - E^{(1)} | \psi^{(1)}_n \rangle \quad (\text{g.ii-26})
\]

Substituting in the definition for \( \psi^{(1)}_n \) from (g.ii-12) will now give

\[
E^{(3)}_n = \sum \sum \frac{\langle \psi^{(0)}_n | \hat{H}^{(1)} - E^{(1)} | \psi^{(0)}_m \rangle \langle \psi^{(0)}_m | \hat{H}^{(1)} - E^{(1)} | \psi^{(0)}_j \rangle}{(E^{(0)}_n - E^{(0)}_m)(E^{(0)}_j - E^{(0)}_j)} \langle \psi^{(0)}_m | H^{(1)} | \psi^{(0)}_n \rangle \quad (\text{g.ii-27})
\]

This is the third order perturbation energy.
J References

1. Conversations with Amy J. Austin.


55. Conversations with Professor Petersson.


