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DISPERSION DIPOLE BETWEEN S-STATE ATOMS

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by

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(Under the supervision of Professor Joseph O. Hirschfelder)

ABSTRACT

When two unlike atoms collide a dipole moment may be induced due to different distortions of their charge clouds. This thesis is concerned with the long-range contribution to this interaction dipole. This contribution can be expanded in a series in R^{-n} in a manner analogous to the long-range interaction energy. We develop an approximation to the first term in this series, D_7. This coefficient is first expressed in a convenient form involving integrals of frequency-dependent properties of the isolated atoms and then an approximate method which involves fairly simple properties of the individual atoms is developed making use of this form. The approximation is tested with accurate variation-perturbation values of D_7 for a model system, for helium-hydrogen, and for helium-helium and is found to be accurate to within 10% or less for these three cases. It is finally used to calculate D_7 for interactions of the rare gas atoms.

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In memory of my mother and father

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1. Introduction

When two molecules or unlike atoms collide, transitions which are ordinarily forbidden may take place due to the distortions of the charge clouds by intermolecular interactions. The absorption of radiation during such transitions is known as collision-induced absorption (CIA).

The first recognized observations of collision-induced absorption were made by Crawford, Welsh, Locke, and MacDonald[1,2,3,19] in 1949 and 1950. They observed ordinarily forbidden vibrational-rotational transitions in O_2, N_2, H_2, and CO_2 at high densities and in H_2 when mixed with foreign gases. Other observations of CIA have also been made[4-6,87,88] including overtones[7] and simultaneous transitions[7,8,27] in both molecules.

Theoretical treatments of CIA soon followed the first experimental work[20-23]. Van Kranendonk and Bird[22,23] considered the usually forbidden 0-1 vibrational band in H_2 and D_2 and distinguished two different mechanisms leading to the induced absorption.

Short-Range Effect. This was called the "atomic distortion effect" since it results from overlap of the molecular charge clouds at short range. This effect is mainly responsible for the Q-branch ($\Delta J_1 = 0$, $\Delta J_2 = 0$) of the 0-1 vibrational rotational spectrum.

Long-Range Effect. This was termed the "quadrupole distortion effect" and results from the polarizing effect of the permanent quadrupole moments of the molecules. It is a long-range effect and goes as R^{-4}. This interaction is primarily responsible for the S ($\Delta J_1 = 2$, $\Delta J_2 = 0$ or $\Delta J_1 = 0$, $\Delta J_2 = 2$) and

O ($\Delta J_1 = -2$, $\Delta J_2 = 0$ or $\Delta J_1 = 0$, $\Delta J_2 = -2$) branches of the vibrational spectrum and is also responsible for one component of the Q-branch.

Calculations of the integrated absorption coefficient were made for H_2, D_2, and H_2-He mixtures and the results obtained were about half the experimental values.

In further theoretical work on pure H_2 and H_2 in mixtures Van Kranendonk has determined a density expansion of the integrated absorption coefficient[24] and calculations have been made of the binary[25,26] and ternary[89] terms in this expansion. In one of these[25] a model was introduced for the interaction dipole which takes into account both the short- and long-range effects mentioned above. It is a four parameter function of which the component along the internuclear axis is

$$\mu(R) = \mu_0 e^{-R/\rho} + \frac{3}{2R^4}\left[\eta_1(3\cos^2\vartheta_1 - 1) - \eta_2(3\cos^2\vartheta_2 - 1)\right]$$

where ϑ_1 and ϑ_2 are the angles of the two molecules with the internuclear axis. The first exponential term is a short-range effect and approximates the dipole due to overlap interactions. The second angular dependent term with R^{-4} dependence is more long-range and approximates the dipole due to dispersion interactions. Van Kranendonk[25] calculated η_1 and η_2 semiempirically and independently of the other two in the asympotic limit as $R \rightarrow \infty$. The μ_0 and ρ parameters were determined from measurements of the total binary absorption coefficient and its temperature dependence. The η_1 and η_2 coefficients can also be calculated using perturbation theory[26].

This dipole function, called the (exp-4) model, has since been used in theoretical calculations of molecular rotational[29] and translational[31] CIA.

Translational absorption, that is absorption due to changes in the relative kinetic energy of the colliding molecules, first became evident in high pressure measurements made by Welsh and co-workers on H_2 and H_2-foreign gas mixtures[9-11]. It was found that the Q-branch of the 0-1 vibrational spectrum was split into three components. One of these is the component due to the long-range quadrupole interactions and is unchanged from low-pressure measurements. The other two arise from the participation of the relative kinetic energies in the absorption process and correspond to an increase or decrease in the relative kinetic energy during the transitions. Under high pressure the molecules are at very short range and the relative motion tends to be of a rotational nature rather than along the line of centers. The two-particle system is then essentially a rigid rotar and the changes in the kinetic energy are like rotational transitions. This leads to two branches of the overlap portion of the Q-branch analogous to those in the infrared rotational-vibrational spectra of diatomic molecules.

Collision-induced pure rotational transitions in H_2 and in H_2-rare gas mixtures have also been observed[12-15, 28,29] and translational effects were again found in this spectra. Kiss, Gush, and Welsh[14] in a study of the absorption intensities for rotational transitions found that the theoretical band intensities were not in good agreement with the experimental values and that the shape of the absorption contours suggested that the rotational lines were overlaid by a continuum in-

creasing in intensity toward lower frequencies. This continuum was interpreted as being a translational one due to collision-induced absorption resulting in changes in the relative kinetic energy. When the experimental curves were separated into rotational and translational parts by a semiempirical method the agreement of the theoretical rotational intensiy with experiment was greatly improved[15].

In order to confirm the existence of purely translational CIA, Kiss and Welsh[16] carried out infrared absorption experiments on compressed mixtures of rare gases and observed the high-frequency tail of a continuous spectrum for helium-neon, helium-argon, and neon-argon. This absorption was attributed to the distortion of the charge distribution of the atoms by intermolecular forces during a collision giving rise to an induced dipole moment. Further measurements were made by Heastie and Martin[17] and the full translational spectrum was obtained in 1965 by Bosomworth and Gush[18] for helium-argon and neon-argon mixtures. No absorption was obtained by the latter authors for helium-neon.

Since this time the theoretical work on CIA has been mainly centered on translational absorption in rare-gas mixtures. The first calculations actually had been done earlier by Buckingham[30] on the interaction dipole. He expressed it in terms of a short-range overlap dipole and a long-range dispersion dipole (which was expanded in a series in R^{-n}, the first term of which was R^{-7}). Approximate calculations were made of the overlap part and of the R^{-7} term in the dispersion part. For HeH he found that they were approximately of the

same magnitude at 5 Bohrs and of opposite sign.

In 1961, Poll and Van Kranendonk[31] developed a theory of the translational integrated absorption coefficient α for atomic and molecular gas mixtures. As in previous calculations[25,29] they expanded the absorption coefficient in terms of densities and calculated the binary term. Their theory begins with a quantum mechanical expression for α and makes the following three approximations:

(1) The interaction dipole is taken to be the overlap form

$$\mu(R) = \mu_0 e^{-R/\rho} ;$$

(2) The interatomic potential is chosen to be the Lennard-Jones (12-6) potential;

(3) The classical form of the pair distribution function is used.

The problem of choosing forms for the interaction dipole and the interatomic potential is one which has been present in all theories of CIA.

After 1965 many theories of the line shape for CIA in rare gas mixtures have been proposed both from quantum mechanical[32,34,36-38] and classical[33,37,39] viewpoints. They differ mainly in the choice of interatomic potential and interaction dipole. The two forms used for the latter have been exponential[32,36,38,39], $\mu(R) = \mu_0 \exp(-R/\rho)$, and modified gaussian[33,34,37], $\mu(R) = \mu_0 \gamma R \exp(-\gamma^2 R^2)$. The gaussian form was chosen mainly for computational convenience[33]. The dipole parameters usually have been fixed by fitting the theoretical expression to the experimental data[18] at the peak of the absorption.

The exponential form, which has been commonly used for the overlap dipole, has received support from Hartree-Fock calculations made by Matcha and Nesbet[35] for HeNe, HeAr, and NeAr. They found that the dipole moments of these molecules could all be fitted by a simple exponential. However the dispersion contribution to the dipole moment could not be obtained by this method since the Hartree-Fock approximation does not describe the correlation effects responsible for dispersion interactions.

Among the line shape theories for CIA mentioned above one of the most recent is that of McQuarrie and Bernstein[39] who calculated the line shape for HeAr in the classical framework of Levine and Birnbaum[33] using the Matcha and Nesbet[35] dipole moment and a Lennard-Jones (12-6) potential. They were able to fit the absorption curve fairly well only if the range (i.e. the ρ parameter) of the dipole was increased by about 10% over that of Matcha and Nesbet.

Levine[40] has tested the exponential model by fitting the two parameters μ_0 and ρ so that two moments of the line shape agree with the experimental values for HeAr and NeAr. He found that the Matcha and Nesbet functions were smaller than these results for two different HeAr potentials and claimed that the disagreement is greater then could be attributed to either the uncertainty in the experimental values or to errors in the Hartree-Fock calculations.

Futrelle has found that the temperature dependence of CIA of rare gas mixtures should be a good method of probing the interaction potential for unlike atoms[42,43]. It was suggested that the problem of the form of the dipole moment can be avoided by determining its form from

a study of the temperature dependence of the shape of the absorption spectrum[42,43].

It is evident from this discussion that one of the important problems in theoretical calculations of CIA is the determination of a reliable functional form for the induced dipole moment. While fairly good theoretical fits to the experimental curves have been obtained for HeAr[38,39] and NeAr[38] using the simple exponential form it is not clear either that better results might not be obtained with another form or that the exponential model will give good results for other pairs.

One obvious area for investigation is the importance of a long-range contribution to the interaction dipole which has been mentioned by Levine[40] as being a possible reason for disagreement of the exponential model with experiment. The dispersion dipole has been treated previously using the Drude model[40] and perturbation theory[30,41]. In one of the latter calculations[41] two terms were annihilated so the results are in error. This thesis will be concerned with this dispersion contribution to the interaction dipole between S-state atoms. The dispersion dipole is expanded in a multipole series in R^{-n} in a manner analogous to the long-range interaction energy and a method proposed for the approximation of the first term in this series which goes as R^{-7}. This approximation is tested with accurate calculations for a model system and for the He-H interaction. It is then finally utilized to obtain the dispersion contribution to the dipole induced in rare-gas interactions[92].

2. Long-Range Dipole Moment

Let us now consider two S-state atoms A and B. We will take the z-axis to be along the internuclear axis and pointing from A to B. The discussion will be limited to large internuclear separations, for which the overlap between the two atoms can be neglected. We will also neglect all retardation effects. If we associate one set of electrons $\{i\}$ with atom A and the remaining electrons $\{j\}$ with atom B the Hamiltonian of the diatom system can be written as

$$\mathcal{H} = H_A(i) + H_B(j) + V \tag{1}$$

where

$$V = -\sum_j \frac{Z_a}{r_{aj}} - \sum_i \frac{Z_b}{r_{bi}} + \sum_{i>j} \frac{1}{r_{ij}} + \frac{Z_a Z_b}{R} \tag{2}$$

and where H_A and H_B are the Hamiltonians of the noninteracting atoms. R is the internuclear separation of the atoms. Since atomic overlap has been neglected the wavefunction of the system need not be antisymmetrized and we can take the zeroth order wavefunction to be a product of the normalized ground state wavefunctions of the isolated atoms, $\Phi_0 = A_0 B_0 \equiv |0\rangle$.

If we let $\mathcal{H}_0 = H_A + H_B$ and $(\mathcal{H}_0 - \mathcal{E}_0)\Phi_0 = 0$ then we can derive a Rayleigh-Schrodinger perturbation expression in terms of the reduced resolvent[45] $\mathcal{R}_0 = (\mathcal{E}_0 - \mathcal{H}_0)^{-1}(1 - |0\rangle\langle 0|)$. If Ψ is the total wavefunction then

$$(\mathcal{H}_0 + V - \mathcal{E})\Psi = 0.$$

Defining $\Delta E = \mathcal{E} - \mathcal{E}_0$ we see that

$$\Psi - \Psi_0 = \mathcal{R}_0 (V - \Delta E) \Psi$$

and that

$$\Psi = [1 - \mathcal{R}_0 (V - \Delta E)]^{-1} \Psi_0 \quad .$$

Expanding the inverse operator[90] and observing that $\mathcal{R}_0 \Psi_0 = 0$ gives

$$\Psi = [1 + \mathcal{R}_0 V + \mathcal{R}_0 (V - \Delta E) \mathcal{R}_0 V + \cdots] \Psi_0 .$$

Since

$$\Delta E = \frac{\langle \Psi_0 | V | \Psi \rangle}{\langle \Psi_0 | \Psi \rangle}$$

$$= \langle \Psi_0 | V | \Psi_0 \rangle + \langle \Psi_0 | V \mathcal{R}_0 V | \Psi_0 \rangle + \cdots$$

we have

$$\Psi = (1 + \mathcal{R}_0 V + \mathcal{R}_0 V' \mathcal{R}_0 V + \cdots) \Psi_0 \tag{3}$$

where $V' = V - \langle \Psi_0 | V | \Psi_0 \rangle$.

The diatom reduced resolvent operator in sum over states form is[45]

$$\mathcal{R}_0 = \sum_k{}' \frac{|k\rangle\langle k|}{\mathcal{E}_0 - \mathcal{E}_k} \tag{4}$$

where $|k\rangle$ is an excited state wavefunction for the isolated diatom system and the summation extends over all discrete states other than $|0\rangle$ and over the continuum.

The perturbation potential V can be expanded in a multipole series[46]

$$V = \sum_{n=1}^{\infty} \frac{V_n}{R^n} \tag{5}$$

where, for the z-axis from atom A to atom B,

$$V_n = \sum_{\ell=0}^{n-1} \sum_{m=-\ell}^{\ell} (-1)^{n-\ell-1} \left[\binom{n-1}{\ell-m} \binom{n-1}{\ell+m} \right]^{1/2} M_\ell^m(i)\, M_{n-\ell-1}^{-m}(j) \tag{6}$$

In this expression M_1^m is an irreducible multipole moment defined by (in atomic units)

$$M_\ell^m = -\sqrt{\frac{4\pi}{2\ell+1}} \sum_i r_i^\ell \, Y_\ell^m(\hat{r}_i) \, . \tag{7}$$

For neutral atoms the first two nonvanishing terms in (5) are V_3 and V_4.

The dipole moment is

$$\mu_{AB} = \frac{\langle \Psi | \mu_0 | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{8}$$

where μ_0 is the dipole moment operator. For two neutral atoms this operator is (in atomic units)

$$\mu_0 = -\sum_i z_i^a - \sum_j z_j^b \, . \tag{9}$$

If we substitute the multipole expansion for V into (3) and the result into (8) we obtain, after collecting the different powers of R,

$$\mu_{AB} = \frac{D_7}{R^7} + \frac{D_9}{R^9} + \cdots \, . \tag{10}$$

The R^{-6} and R^{-8} terms vanish because of symmetry. The D_7 coefficient is given by

$$D_7 = 2 \langle 0 | \mu_0 R_0 V_3 R_0 V_4 + \mu_0 R_0 V_4 R_0 V_3 + V_3 R_0 \mu_0 V_4 | 0 \rangle . \tag{11}$$

If the excited states $|k\rangle$ of the diatom are expressed as a product of states of the two isolated atoms, $|k\rangle = |A_k B_\ell\rangle$, then the reduced resolvent may be written

$$\mathcal{R}_0 = \sum_{k\neq 0} \frac{|A_k B_0\rangle\langle A_k B_0|}{E_0^A - E_k^A} + \sum_{\ell\neq 0} \frac{|A_0 B_\ell\rangle\langle A_0 B_\ell|}{E_0^B - E_\ell^B} + \sum_{k\neq 0}\sum_{\ell\neq 0} \frac{|A_k B_\ell\rangle\langle A_k B_\ell|}{E_0^A + E_0^B - E_k^A - E_\ell^B} \quad . \tag{12}$$

Defining a single atom frequency dependent resolvent

$$R_0^A(\omega) = -\sum_{k\neq 0} \frac{(E_k^A - E_0^A)|A_k\rangle\langle A_k|}{(E_k^A - E_0^A)^2 + \omega^2} \tag{13}$$

and making use of the identity[47]

$$\frac{1}{a+b} = \int_{-\infty}^{\infty} \frac{d\omega}{\pi}\left(\frac{a}{a^2+\omega^2}\right)\left(\frac{b}{b^2+\omega^2}\right) \qquad (a,b>0) \tag{14}$$

we can express $\mathcal{R}_0$ in a more convenient form

$$\mathcal{R}_0 = |B_0\rangle\langle B_0| R_0^A + |A_0\rangle\langle A_0| R_0^B + R_0^{AB}. \tag{15}$$

In this expression, $R_0^A = R_0^A(0)$ and R_0^{AB} is a "double excitation" resolvent

$$R_0^{AB} = \sum_{k\neq 0}\sum_{\ell\neq 0} \frac{|A_k B_\ell\rangle\langle A_k B_\ell|}{E_0^A + E_0^B - E_k^A - E_\ell^B} \quad . \tag{16}$$

After extensive symmetry reduction summarized in Appendix A equation (11) is reduced to the following form

$$D_\eta = D_\eta^{I} + D_\eta^{II} \tag{17}$$

$$D_7^{I} = q\int_{-\infty}^{\infty} \frac{d\omega}{\pi}\left[\alpha_A(i\omega)\gamma_B(\omega) - \alpha_B(i\omega)\gamma_A(\omega)\right] \tag{18}$$

$$D_7^{II} = q\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{du\,dv}{\pi^2}\left[L_A(u,v)\Gamma_B(u,v) - L_B(u,v)\Gamma_A(u,v)\right] \tag{19}$$

where

$$\alpha(i\omega) = -2\langle 0|\mu R_0(\omega)\mu|0\rangle \tag{20}$$

$$\gamma(\omega) = -\langle 0|\mu R_0 \Theta R_0(\omega)\mu + \mu R_0 \mu R_0(\omega)\Theta|0\rangle \tag{21}$$

$$\Gamma(u,v) = -\langle 0|\mu R_0(u)\mu R_0(v)\Theta|0\rangle \tag{22}$$

$$L(u,v) = 2\langle 0|\mu R_0(u) R_0(v)\mu|0\rangle \ . \tag{23}$$

In (20) through (23) μ and Θ are the m = 0 components of the dipole and quadrupole moments, $\mu = M_1^0$ and $\Theta = M_2^0$. The resolvent R_0 (w) is defined by equation (13). We have redefined $|0\rangle$ to be the ground state atomic wavefunction for A or B.

3. Approximate Formula for D_7

Of the four quantities defined by (20) - (23) only one is well-known - $\alpha(i\omega)$, the frequency-dependent polarizability. The others can be related to known properties only in the static limit. For spherical systems Buckingham[48] has defined a scalar $B^{(0)}$ which is the coefficient of the electric field squared times the electric field gradient in the expansion of the energy in an electric field. It is

found that

$$B^{(o)} = -2\left[\gamma(o) + \Gamma(o,o)\right] . \tag{24}$$

One measurement of $B^{(o)}$ has been made for methane[48]. Also, we see that L(o,o) is the dipole sum[49] S(-3).

Since frequency-dependent values of γ, L, and Γ are not available from experiment and also are difficult to calculate for atoms much larger than helium it would be useful to develop approximations for them. One method which has been used in the past is the Unsöld approximation[30,50]. In this approximation all excitation energies $E_k - E_o$ in the resolvent (13) are replaced by a single average excitation energy E. Then $R_o(w)$ becomes

$$R_o(\omega) \approx \frac{E\,(|o\rangle\langle o| - 1)}{E^2 + \omega^2} . \tag{25}$$

If we substitute (25) into equations (20) - (23) for α, γ, Γ, and L and the results into (18) and (19), carrying out the integrations gives us

$$D_7 \approx 18(1-P_{AB})\left[\frac{\langle o|\mu^2 \otimes |o\rangle_A \langle o|\mu^2|o\rangle_B}{(E_A + E_B)}\left(\frac{2}{E_A} + \frac{1}{E_A+E_B}\right)\right] \tag{26}$$

The operator P_{AB} permutes the subscripts A and B.

Different choices of E are possible. Three of these are: (i) the ionization energy I of the atom; (ii) the dipole polarizability average excitation energy

$$\epsilon = \frac{2\langle o|\mu^2|o\rangle}{\alpha_o} \tag{27}$$

(iii) the quadrupole polarizability average excitation energy

$$\epsilon_{\Theta} = \frac{2\langle 0|\Theta^2|0\rangle}{\alpha_{\Theta}} \tag{28}$$

where

$$\alpha_{\Theta} = -2\langle 0|\Theta R_0 \Theta|0\rangle \quad . \tag{29}$$

Buckingham chose the first. We choose the dipole polarizability average excitation energy ϵ because it gives the most accurate approximations to the exact values of $\gamma(0)$, $\Gamma(0,0)$, and $L(0,0)$ for the hydrogen atom.

The Unsöld approximation, while simple to use, is not very accurate for the model system presented in the next section. Another apparently more accurate approximation scheme can be developed as follows.

First, let us consider D_7^I and write it as

$$D_7^I = 9\int_{-\infty}^{\infty} \frac{d\omega}{\pi} \alpha_A(i\omega)\alpha_B(i\omega)\left[\frac{\gamma_B(\omega)}{\alpha_B(i\omega)} - \frac{\gamma_A(\omega)}{\alpha_A(i\omega)}\right] . \tag{30}$$

If we then assume that $\gamma(\omega)/\alpha(\omega)$ is a constant g^I and utilize the expression for the Van der Waals coefficient C_6^{AB} as an integral over dynamic polarizabilities[49] we obtain

$$D_7^I \approx 6\, C_6^{AB} (g_B^I - g_A^I) . \tag{31}$$

In the same manner, let

$$D_7^{II} \approx 9\, C_{AB}^{II} (g_B^{II} - g_A^{II}) \tag{32}$$

where we have assumed that $\frac{\Gamma(u,v)}{L(u,v)}$ is a constant g^{II} and have defined

$$C^{II}_{AB} = \iint_{-\infty}^{\infty} \frac{du\,dv}{\pi^2} L_A(u,v) L_B(u,v) . \tag{33}$$

The problem is now reduced to calculating C^{II}_{AB} and choosing values for g^{I} and g^{II}. Various choices are available for the latter two, the most obvious being the values obtained by taking the zero or infinite frequency limits of the ratios $\gamma(\omega)/\alpha(i\omega)$ and $\Gamma(u,v)/L(u,v)$. However, reasonable and computationally convenient forms result if we define the "frequency average" of a quantity $B(u,v,w,\ldots)$ to be

$$\overline{B} = \int_{-\infty}^{\infty} \frac{du}{\pi} \int_{-\infty}^{\infty} \frac{dv}{\pi} \cdots \int_{-\infty}^{\infty} \frac{d\omega}{\pi} B(u,v,\ldots,\omega) \tag{36}$$

and let the constants be

$$g^{I} = \frac{\overline{\gamma}}{\overline{\alpha}} \tag{37}$$

and

$$g^{II} = \frac{\overline{\Gamma}}{\overline{L}} . \tag{38}$$

We will use (37) and (38) as our choice of the constant values for g^{I} and g^{II}. This is discussed further in Appendix B. The frequency averaged quantities needed are

$$\overline{\alpha} = 2\langle 0|\mu^2|0\rangle \tag{40}$$

$$\bar{\gamma} = 2\langle 0|\mu R_0 \mu \Theta|0\rangle \tag{41}$$

$$\bar{\Gamma} = -\langle 0|\mu^2 \Theta|0\rangle \tag{42}$$

$$\bar{L} = 2\langle 0|\mu^2|0\rangle \quad . \tag{43}$$

For this choice we need only calculate two expectation values and one second-order property. The latter should not be much more difficult to do than the static polarizability.

We are still left with C_{AB}^{II}, a quantity not too different from the Van der Waals coefficient C_6^{AB}, as is most easily seen from their sum-over-states form

$$C_{AB}^{II} = \sum_k{}' \sum_\ell{}' \frac{f_{k0}^a f_{\ell 0}^b}{\omega_{k0}^a \omega_{\ell 0}^b (\omega_{k0}^a + \omega_{\ell 0}^b)^2} \tag{44}$$

$$C_6^{AB} = \frac{3}{2} \sum_k{}' \sum_\ell{}' \frac{f_{k0}^a f_{\ell 0}^b}{\omega_{k0}^a \omega_{\ell 0}^b (\omega_{k0}^a + \omega_{\ell 0}^b)} \quad . \tag{45}$$

Because of this similarity it should be possible to use methods[51,52] developed for C_6^{AB} as a means of calculating C_{AB}^{II}. Simple approximations can also be made. For example in equation (44) let $(\omega_{k0}^a + \omega_{\ell 0}^b)^2 = (\epsilon_A + \epsilon_B)^2$ where ϵ_A and ϵ_B are average dipole polarizability excitation energies. Since the oscillator strength is $f_{k0} = 2\omega_{k0} |\langle 0|\mu|k\rangle|^2$, the identity

$$\sum_k{}' \frac{f_{k0}}{\omega_{k0}} = 2\langle 0|\mu^2|0\rangle = \bar{\alpha} \tag{46}$$

can be used to give

$$C^{II}_{AB} \approx \frac{\bar{\alpha}_A \bar{\alpha}_B}{(\epsilon_A + \epsilon_B)^2} \quad . \tag{47}$$

If instead in (44) we take $(w^a_{ko} + w^b_{lo})^2 = (w^a_{ko} + w^b_{lo})(\epsilon_A + \epsilon_B)$ and consider equation (45) we have a second approximation for C^{II}_{AB}

$$C^{II}_{AB} \approx \frac{2\, C^{AB}_6}{3(\epsilon_A + \epsilon_B)} \quad . \tag{48}$$

For two hydrogen atoms (47) is 5.063 and (48) is 4.874. These are quite close (3% for the first and 1% for the second) to an accurate value of 4.9324 calculated in the next section.

It should be noted that if we choose (47) as our value of C^{II}_{AB} then the D^{II}_7 which results is the same as that from the Unsöld approximation. In fact if Unsöld values of C^{AB}_6 and $\bar{\gamma}$ are also used

$$C^{AB}_6 \approx \frac{3\bar{\alpha}_A \bar{\alpha}_B}{2(\epsilon_A + \epsilon_B)} \tag{49a}$$

$$\bar{\gamma} \approx \frac{2}{\epsilon} \langle 0 | \mu^2 \Theta | 0 \rangle \tag{49b}$$

our approximation (31) and (32) reduces to the Unsöld form of equation (26).

4. Model System: Scaled Hydrogen Atoms

A simple system for which it is possible to calculate an accurate D_7 as a test of our approximation is that of a scaled hydrogen atom interacting with a hydrogen atom. The accurate treatment utilizes a variation-perturbation technique previously used by others for the

calculation of long-range energies[53,54] and frequency-dependent properties[55].

For an atom A, we choose an orthonormal set $\{\tilde{A}_k\}$ such that $\tilde{A}_0 = A_0$, the exact ground state wavefunction, and such that the unperturbed Hamiltonian matrix is diagonal, $\langle \tilde{A}_k | H_A - E_0^A | \tilde{A}_\ell \rangle = \Delta\epsilon_k^A \delta_{k\ell}$. An approximation for the resolvent (13) in terms of this basis is

$$R_0^A(\omega) \approx -\sum_{k=1}^{N} \frac{\Delta\epsilon_k^A |\tilde{A}_k\rangle\langle\tilde{A}_k|}{(\Delta\epsilon_k^A)^2 + \omega^2} . \tag{50}$$

If we substitute (50) into equations (20) - (23) for α, γ, Γ, and L and the results into (18) and (19), carrying out the integrations gives us

$$D_\eta^{I} = -18(1-P_{AB}) \sum_{k=1}^{N}\sum_{\ell=1}^{N}\sum_{m=1}^{N} \frac{|\mu_{k0}^A|^2 \mu_{0\ell}^B (\mu_{\ell m}^B \Theta_{m0}^B + \Theta_{\ell m}^B \mu_{m0}^B)}{\Delta\epsilon_\ell^B (\Delta\epsilon_k^A + \Delta\epsilon_m^B)} \tag{51}$$

$$D_\eta^{II} = -18(1-P_{AB}) \sum_{k=1}^{N}\sum_{\ell=1}^{N}\sum_{m=1}^{N} \frac{|\mu_{k0}^A|^2 \mu_{00}^B \mu_{\ell m}^B \Theta_{m0}^B}{(\Delta\epsilon_k^A + \Delta\epsilon_\ell^B)(\Delta\epsilon_k^A + \Delta\epsilon_m^B)} \tag{52}$$

where

$$\mu_{k\ell}^A = \langle \tilde{A}_k | \mu | \tilde{A}_\ell \rangle \quad , \quad \Theta_{k\ell}^A = \langle \tilde{A}_k | \Theta | \tilde{A}_\ell \rangle \tag{53}$$

and similarly for B.

For the hydrogen-scaled hydrogen model system the zeroth-order wavefunctions are

$$A_0 = \sqrt{\frac{\zeta^3}{\pi}}\, e^{-\zeta r} \qquad B_0 = \frac{1}{\sqrt{\pi}}\, e^{-r} . \tag{54}$$

As initial basis sets for the two atoms we choose the orbitals of Löwdin and Shull[56,57] with a unit scaling factor for atom B. The basis sets $\{A_k\}$ and $\{B_k\}$ are formed by diagonalizing the Hamiltonians of A_o and B_o with the respective Löwdin-Shull basis set. Practically, only two symmetry types of these need be used - those of p and d angular symmetry. Basis sets of 10 p-and 20 d-orbitals were found to give satisfactory convergence. The accurate results from (51) and (52) are in Tables 2 and 3.

Since the first order wavefunction $R_{o\mu}\Psi_o$ is known exactly for one-electron systems[58] the approximations (31) and (32) can be easily calculated using the frequency-averaged values for g^I and g^{II}. The necessary constants C_6^{AB} and C_{AB}^{II} are computed using the accurate technique described above. The expressions for these constants are

$$C_6^{AB} = 6 \sum_{k=1}^{N} \sum_{\ell=1}^{N} \frac{(\mu_{k0}^A)^2 (\mu_{\ell 0}^B)^2}{\Delta\epsilon_k^A + \Delta\epsilon_\ell^B} \tag{54}$$

$$C_{AB}^{II} = 4 \sum_{k=1}^{N} \sum_{\ell=1}^{N} \frac{(\mu_{k0}^A)^2 (\mu_{\ell 0}^B)^2}{(\Delta\epsilon_k^A + \Delta\epsilon_\ell^B)^2} \quad . \tag{55}$$

The accurate C_6^{AB} and C_{AB}^{II} calculated in this manner for scaling factors from one to two are listed in Table 1 along with the two approximations (47) and (48). The results from approximations (31) and (32) are in Tables 2 and 3. Also in Table 3 we have included the results of the Unsöld Approximation (26).

Checks on the completeness of the basis used for hydrogen may be found in Appendix D. Some properties of the finite basis set are in Appendix H.

5. Discussion: Model System

From Table 3 it is seen that the agreement between the accurate and our approximate values of D_7 is quite good, being about 1.5% for $\zeta = 1$ to $\zeta = 2$. For this model system, at least, our approximation is superior to the Unsöld and very close to the accurate method.

In Table 1 the simple approximations (47) and (48) to C_{AB}^{II} do seem to be satisfactory. Furthermore, in Table 2 we see that D_7^{II} is about an order of magnitude smaller than D_7^{I} so that, even if C_{AB}^{II} is not known precisely, we may still be able to obtain a good approximation to D_7 if D_7^{I} is fairly accurate.

For this model system we knew the first order wavefunction $R_0 \mu \Psi_0$ exactly and hence were able to obtain an exact value for $\bar{\gamma}$. Unfortunately, this will not be true for more complex systems. This indicates that the most important problem in this approximation scheme is the calculation of $\bar{\gamma} = 2\langle 0|\mu R_0 \mu \Theta|0\rangle$ as accurately as possible in order to have a good value of D_7^{I}.

6. Calculation of $\bar{\gamma}$

An accurate value of $\bar{\gamma}$ is difficult to obtain because of the presence of the resolvent operator. A very simple method of approximating $\bar{\gamma}$ is the Unsöld Approximation which lets the resolvent be $R_0 \approx -\frac{1}{\epsilon}$ and gives

$$\bar{\gamma} \approx -\frac{2\langle 0|\mu^2 \Theta|0\rangle}{\epsilon} \tag{56}$$

Since the Unsöld approximation for D_7 was found in Sections 4 and 5 to be relatively inaccurate for the model system it would seem desirable to avoid using it for $\bar{\gamma}$ if at all possible.

A second approximation may be formulated as in the He polarizability calculations of Baber and Hasse[59,60]. They let $\tilde{\Psi}^{(1)}$ be a two-term approximation to $R_{0\mu}\Psi_0$ where

$$\tilde{\Psi}^{(1)} = \sqrt{\frac{4\pi}{3}} \sum_{\lambda=1}^{N_e} (c_1 r_\lambda + c_2 r_\lambda^3) Y_1^0(\lambda) \Psi_0 \tag{57}$$

and where N_e= number of electrons. If $C_1 = \frac{1}{\epsilon}$ and $C_2 = 0$ this is just the Unsöld approximation. However let us determine C_1 and C_2 by extremizing the functional

$$J = \langle \tilde{\Psi}^{(1)} | H_0 - E_0 | \tilde{\Psi}^{(1)} \rangle + 2 \langle \tilde{\Psi}^{(1)} | \mu | \Psi_0 \rangle \tag{58}$$

where $(H_0 - E_0)\Psi_0 = 0$. Then using $\tilde{\Psi}^{(1)}$ in (41) gives a new approximation

$$\bar{\gamma} \approx \langle \tilde{\Psi}^{(1)} | \mu \Theta | \Psi_0 \rangle . \tag{59}$$

This is the exact expression for $\bar{\gamma}$ [58] for a one-electron atom. A more detailed explanation of the calculation of $\bar{\gamma}$ may be found in Appendix E.

Other methods commonly used for polarizabilities should also be appropriate for $\bar{\gamma}$. Dalgarno's review article[58] covers them quite well. Probably the most useful of these for more complex systems would

be uncoupled Hartree-Fock perturbation theory[61]. However if we compare rare gas polarizabilities calculated with the two-term first order wavefunction (57) using Clementi's[62] Hartree-Fock Ψ_0 and uncoupled Hartree-Fock polarizabilities (Table 4) we see that the two-term values are as good as or better than the uncoupled Hartree-Fock. This coupled with the relative simplicity of (59) makes the two-term approximation to $\bar{\gamma}$ quite attractive.

7. Approximation: He-H and He-He

We have now formulated a method of approximating D_7 which has been successful for a simple model system. The next step is to test this method for two more realistic systems, He-H and He-He. This will serve two purposes - a further check of the accuracy of the method and also a test of the two ways of calculating $\bar{\gamma}$ given in (56) and (59).

Approximation 1

This is the approximation proposed in equations (31), (32), and (40) - (43). All quantities including $\bar{\gamma}$ and C_{AB}^{II} will be calculated accurately using the methods described previously for hydrogen and in the next section for helium. This will serve as a check on the validity of the approximation procedure.

Approximation 2

This is the same as the first except that $\bar{\gamma}$ is determined using the two-term approximation (59). In calculating constants

C_1 and C_2 by the functional (58), the substitution of equation (63) was made.

Approximation 3

This is the same as the first except that $\bar{\gamma}$ is calculated using the Unsöld method of equation (56).

Approximation 4

This is the Unsöld approximation for D_7 of equation (26). The hydrogen expectation values used are exact. Those needed for helium are done accurately using the Hart-Herzberg[64] wavefunction.

The values of $\bar{\gamma}$ and g^I used in the first three approximations are compared in Table 5. In Tables 6 and 7 we have listed the results of the four approximations for He-H and He-He along with accurate values calculated in the next section. For He-He only the one-way coefficients $\vec{D}_7 = \vec{D}_7^{I} + \vec{D}_7^{II}$ are tabulated, where

$$\vec{D}_7^{I} = q\int_{-\infty}^{\infty} \frac{d\omega}{\pi}\, \alpha_{He}(i\omega)\, \gamma_{He}(\omega) \tag{60}$$

$$\vec{D}_7^{II} = q\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{du\,dv}{\pi^2}\, L_{He}(u,v)\, \Gamma_{He}(u,v). \tag{61}$$

The total coefficient vanishes for interactions of identical atoms.

8. Accurate Calculations: He-H and He-He

An accurate calculation of D_7 for a hydrogen-scaled hydrogen system was discussed in Section 4. The same variation-perturbation

method can be applied to the He-H and He-He interactions. The exact hydrogenic wavefunction and Löwdin-Shull orbital basis may be used for hydrogen as in Section 4.

For helium we choose, as have others[54,63], the 20-term Hart-Herzberg[64] wavefunction as Ψ_0 and the initial basis set Ψ nlm = Fnlm Ψ_0 , where

$$F_{nlm} = \sum_{i=1}^{2} r_i^n Y_l^m(\hat{r}_i) \qquad n \geq l \, . \tag{62}$$

This set must be made simultaneously orthonormal and diagonal with respect to the helium Hamiltonian in order to be used in the accurate calculation like that described in Section 4. Because of symmetry we again need only consider subsets for which m = 0 and l = 1 and 2. These subsets were each of six basis orbitals since larger sets led to a loss of accuracy in the orthonormalization step. As usual[54,63] the substitution

$$\langle 0 | F_{nlm} (H_0 - E_0) F_{n'l'm'} | 0 \rangle \approx \frac{1}{2} \sum_{i=1}^{N_e} \langle 0 | \nabla_i F_{nlm} \cdot \nabla_i F_{n'l'm'} | 0 \rangle \tag{63}$$

was made.

The accurate results for He-H and He-He are also given in Tables 6 and 7. In Appendix F will be found a short description of the He atom calculation and in Appendix H some properties of the basis sets.

9. Discussion: He-H and He-He

The results for He-H and He-He confirm those for hydrogen. The proposed approximation is better than the Unsöld and can be quite good,

at least for small atoms. The He-He case, in which it is about 10% off, is the best indication of the accuracy which might be expected for larger atoms.

It is also clear that our approximation with the two-term $\overline{\gamma}$ is a definite improvement over the Unsöld $\overline{\gamma}$. In fact, for helium, (59) gives $\overline{\gamma}$ accurate to at least three figures. This is a sign that the two-term $\overline{\gamma}$ is good enough to use for more complex atoms. We are further encouraged by the fact that Pople and Schofield[65] have found that for argon this representation of $R_{0\mu}\Psi_0$ is a close approximation to the optimum form $R_{0\mu}\Psi_0 \approx \sum_i u(r_i)\Psi_0$ where Ψ_0 is a numerical Hartree-Fock wavefunction[66].

Since the proposed approximation for D_7 has also behaved well for He-H and He-He it would seem that calculations for the rare gas atoms would be worthwhile. However, before doing this, we will look at an interpolation method for obtaining accurate values of C_{AB}^{II}.

10. Sum Rule Interpolation for C_{AB}^{II}

While approximations (47) and (48) are available for C_{AB}^{II} we would like to have a method of obtaining it more accurately for large atoms. One relatively simple method is an adaptation of Bell's technique[51] for C_6^{AB} which requires only knowledge of the dipole sum rules for the two atoms in question.

Following Bell[51] we can write

$$C_{AB}^{II} \approx \sum_{i=2}^{6}\sum_{j=2}^{6} C_{ij} E^{i+j-4} S^A(-i)\, S^B(-j) \tag{64}$$

where S(n) is the sum

$$S(n) = \sum_{k}{}' \omega_{k0}^{n} f_{k0} \tag{65}$$

and E = minimum of the two ground to first excited state dipole transition energies for atoms A and B.

The constants C_{ij} are chosen so that

$$\frac{x^3 y^3}{(x+y)^2} = \sum_{i=2}^{6} \sum_{j=2}^{6} C_{ij} x^i y^j \tag{66}$$

is satisfied exactly for selected values of (x,y). We have chosen these points to be Bell's most successful set

$$(x,y) = \left(\frac{r}{5}, \frac{s}{5}\right) \qquad r,s = 0,1,\ldots,5 . \tag{67}$$

The C_{ij} determined in this manner are given in Table 8.

Barker and Leonard[67] quote the sum rules S(0), S(-1), S(-2), S(-4), and S(-6) for the rare gas atoms. To obtain S(-3) and S(-5) we use the interpolation formula of Bell

$$\ln\left[\frac{S(k)}{S(0)}\right] = k\left[a + \frac{b}{5-2k} + \frac{c}{(5-2k)^2} + \frac{d}{(5-2k)^3}\right] . \tag{67a}$$

The constants a,b,c, and d are determined from the known sum rules. The sum rules used for our interpolation of C_{AB}^{II} are in Table 9. We also have listed those of hydrogen and those calculated for helium as in Section 8. As a check on the accuracy of the sum rule interpolation the interpolated values for hydrogen are S(-3) = 10.7504 (10.7500) and S(-5) = 67.170 (67.174) with exact values[49] in parentheses.

Having obtained the necessary sum rules we have calculated C_{AB}^{II} according to equation (64) using the values of E from Moore[68]. The results are in Table 11. We have also interpolated C_{AB}^{II} for hydrogen and helium using the exact sum rules for hydrogen and the Hart-Herzberg sum rules for helium. These can be compared with the values of C_{AB}^{II} previously calculated in Sections 4 and 8 as a consistency check on the interpolation procedure. The results are in Table 10.

11. Rough Approximation: Rare Gas Atoms

The next step is the calculation of D_7 for the rare gas atoms using the sum rule interpolated C_{AB}^{II} and Hartree-Fock evaluation of necessary expectation values. First, we would like to present a rough method of estimating D_7 which should illustrate how sensitive the approximations are and which also might be useful in obtaining order-of-magnitude estimates for other atoms.

This approximation draws upon one made earlier by Buckingham[30]. If we use the two-term approximation for $\overline{\gamma}$ we will need to evaluate the three integrals (summations over electrons)

$$\langle 0|\mu^2|0\rangle = \frac{4\pi}{3}\sum_{ij}\langle 0|r_i r_j Y_1^0(\hat{r}_i)Y_1^0(\hat{r}_j)|0\rangle \tag{68}$$

$$\langle 0|\mu^2\Theta|0\rangle = -\frac{4\pi}{3}\sqrt{\frac{4\pi}{5}}\sum_{ijk}\langle 0|r_i r_j r_k^2 Y_1^0(\hat{r}_i)Y_1^0(\hat{r}_j)Y_2^0(\hat{r}_k)|0\rangle \tag{69}$$

$$\langle 0|\mu R_0 \mu\Theta|0\rangle \approx -C_1\langle 0|\mu^2\Theta|0\rangle + C_2\frac{4\pi}{3}\sqrt{\frac{4\pi}{5}}\sum_{ijk}\langle 0|r_i^2 r_j r_k^2 Y_1^0(\hat{r}_i)Y_1^0(\hat{r}_j)Y_2^0(\hat{r}_k)|0\rangle . \tag{70}$$

If we neglect all cross-terms in the summations these reduce to

$$\langle 0|\mu^2|0\rangle \approx \frac{1}{3}\sum_i \langle 0|r_i^2|0\rangle \tag{71}$$

$$\langle 0|\mu^2\Theta|0\rangle \approx -\frac{2}{15}\sum_i \langle 0|r_i^4|0\rangle \tag{72}$$

$$\langle 0|\mu R_0\mu\Theta|0\rangle \approx \frac{2}{15}\sum_i \left[C_1\langle 0|r_i^4|0\rangle + C_2\langle 0|r_i^5|0\rangle\right]. \tag{73}$$

This reduction is helpful since the Hartree-Fock expectation values $\sum_i \langle 0|r_i^n|0\rangle$ have been tabulated for $n \leq 5$ by Fraga and Malli[69]. The rare gas expectation values are quoted in Table 12.

This rough approximation will utilize (71) - (73) in the calculation of g^I and g^{II} and in the approximation of C_{AB}^{II} by (47). Literature values[52] will be used for C_6^{AB}. We have listed the values of C_{AB}^{II} from (47) in Table 13. The results of the rough approximation for D_7 are to be found in Table 14.

12. Full Approximation: Rare Gas Atoms

To complete our treatment we have calculated the ground state expectation values (68) - (70) for He, Ne, Ar, and Kr with Clementi's analytical Hartree-Fock wavefunctions[62]. The values of $\langle 0|\mu^2|0\rangle$ and $\langle 0|\mu^2\Theta|0\rangle$ obtained are listed in Table 15 along with their approximations (71) and (72). With these expectation values and those of $\sum_i r_i^n$ we can calculate the constants C_1 and C_2 for $\langle 0|\mu R_0\mu\Theta|0\rangle$ and hence $\bar{\gamma}$, g^I, and g^{II}. These constants are given in Table 16 along with those for hydrogen and for helium calculated with the Hart-Herzberg wavefunction. The two-term polarizabilities in Table 4

were calculated with these values of C_1 and C_2.

With the values of g^I and g^{II} in Table 16, the sum rule interpolated C_{AB}^{II} in Table 11, and C_6^{AB} from Dalgarno[52] we have calculated D_7 for hydrogen and the rare gas atoms. The results are listed in Tables 17, 18, and 19 (the Hart-Herzberg constants were used for helium).

13. Discussion: Rare Gas Atoms

First, the sum rule interpolated C_{AB}^{II} constants should be accurate to at least 5%. This estimate is based upon the agreement of Bell's[51] sum rule interpolated C_6 coefficients with other methods[52,67,70,71] for the rare gases. Since C_6 and C_{AB}^{II} are very similar there is no reason to suspect that they shouldn't be of approximately the same accuracy.

The rough approximates to D_7 in Table 14 mostly differ from the Hartree-Fock values in Table 19 by 20-50%. The differences are greater for the larger atoms with the NeAr and NeKr estimates being about twice the Hartree-Fock values. This method seems suitable for quick estimates of D_7 where not too much accuracy is required.

It is difficult to judge the accuracy of the D_7 coefficients in Table 19 since errors can arise both from the approximation procedure itself and from the calculation of the expectation values $\langle 0|\mu^2|0\rangle$, $\langle 0|\mu^2\Theta|0\rangle$, and $\bar{\gamma}$. The accurate H and He calculations suggest that the approximation procedure is good to 10% or less given accurate expectation values. For the other rare gas atoms we don't have these.

However, if we observe the expectation values for the two Helium calculations (Hart-Herzberg and Hartree-Fock) in Tables 15 and 16 we see that accurate expectation values may not be absolutely necessary. The Hartree-Fock values of $\langle 0|\mu^2|0\rangle$, $\langle 0|\mu^2\Theta|0\rangle$, and $\bar{\gamma}$ all differ from the accurate ones by about 5% but g^{I} and g^{II} for the two are the same to less than a percent.

It is also of interest to compare the values of D_7/R^7 with the corresponding overlap dipoles. This is done in Table 20 for some overlap values available. It seems that the magnitude of D_7/R^7 is comparable to that of the overlap dipole for HeH and HeNe but is 5 to 10 times smaller for HeAr and NeAr. Except for HeNe the overlap and D_7 contributions oppose each other.

14. Conclusions

We have developed an approximation for the first term in the R^{-n} expansion of the dispersion contribution to the interaction dipole for S-state atoms. This approximation is close to the accurate values for hydrogen and helium and is applicable to larger atoms although it is not as easy to gauge the accuracy for these. At the very least, the values of D_7 obtained should be of the correct order of magnitude.

In the four cases in which estimates of the overlap dipole are available we have found that the dispersion dipole is smaller. However, the two contributions are comparable in magnitude for HeH and HeNe and are of the opposite sign for all except HeNe.

In the classical calculation of McQuarrie and Bernstein[39] the overlap dipole function of Matcha and Nesbet[35] for HeAr was too small

to fit the experimental absorption curve well. Levine[40] obtained a similar result for HeAr and NeAr when he compared two theoretical moments of the absorption spectrum calculated using the Matcha and Nesbet dipole with those from experiment. It was conjectured in both cases that one factor which might have led to this disagreement with experiment was the neglect of the dispersion contribution. Since the overlap and dispersion dipoles for HeAr and NeAr are of opposite sign the long-range contributions do not seem to account for the discrepancy. In fact, the addition of a dispersion contribution will make the dipole even smaller because of this sign difference. This effect might not be large for these two cases because of the small value of D_7.

Since we have found that for some cases the R^{-7} dispersion contribution to the interaction dipole is comparable to the overlap it would seem that a three-parameter function of a form such as

$$\mu(R) = A e^{-R/\rho} + \frac{B}{R^7} \tag{74}$$

would be a more accurate general description of the dipole moment than the simple exponential[40]. A form similar to this with a R^{-4} long-range contribution has been used for intermolecular interactions[31]. For diatom systems such as HeH and HeNe in which the dispersion contribution is relatively large this three-parameter dipole function may be necessary to obtain accurate theoretical collision-induced absorption curves.

APPENDICES

A. Symmetry Reduction of D_7

Equation (11) for D_7 is

$$D_7 = 2\langle 0|\mu_0 R_0 V_3 R_0 V_4 + \mu_0 R_0 V_4 R_0 V_3 + V_3 R_0 \mu_0 R_0 V_4|0\rangle \tag{A1}$$

where

$$|0\rangle = |A_0 B_0\rangle \tag{A2}$$

$$R_0 = |B_0\rangle\langle B_0| R_0^A + |A_0\rangle\langle A_0| R_0^B + R_0^{AB} \tag{A3}$$

$$V_3 = -(2\mu_0^a \mu_0^b + \mu_+^a \mu_-^b + \mu_-^a \mu_+^b) \tag{A4}$$

$$V_4 = V_4^{ab} - V_4^{ba} \tag{A5}$$

$$V_4^{ab} = 3\mu_0^a \mu_0^b + \sqrt{3}\,(\mu_{+1}^a \Theta_{-1}^b + \mu_{-1}^a \Theta_{+1}^b) \tag{A6}$$

and

$$\mu_0 = \mu_0^a + \mu_0^b \quad . \tag{A7}$$

In (A4) through (A7)

$$\mu_m = M_1^m = -\sqrt{\frac{4\pi}{3}} \sum_i r_i Y_1^m(\hat{r}_i) \tag{A8}$$

$$\Theta_m = M_2^m = -\sqrt{\frac{4\pi}{5}} \sum_i r_i^2 Y_2^m(\hat{r}_i) \tag{A9}$$

where the summations are over the electrons in the atom.

The first part of the reduction is by symmetry and is the same for all three terms of D_7. Let us consider only the first, $\langle 0|\mu_0 R_0 \cdot V_3 R_0 V_4|0\rangle$, as an example. Substitute (A5) and (A7) into it.

$$\langle 0|\mu_0 R_0 V_3 R_0 V_4|0\rangle = \langle 0|(\mu_0^a + \mu_0^b) R_0 V_3 R_0 (V_4^{ab} - V_4^{ba})|0\rangle. \tag{A10}$$

First, if we notice that μ_0, V_3, and V_4^{ab} are of the symmetry $Y_1^0(a) + Y_1^0(b)$, $Y_1^m(a)Y_1^{m'}(b)$, and $Y_1^m(a)Y_2^m(b)$ and that the resolvents R_0 are spherically symmetric we see that only two terms of (A10) survive

$$\langle 0|\mu R_0 V_3 R_0 V_4|0\rangle = (1 - P_{ab})\langle 0|\mu_0^b R_0 V_3 R_0 V_4^{ab}|0\rangle. \tag{A11}$$

The operator P_{ab} permutes the superscripts a and b. If we then substitute the explicit forms (A4) and (A6) for V_3 and V_4^{ab} into (A11) and retain only the non zero terms (for which $\Sigma m = o$) we obtain

$$\langle 0|\mu R_0 V_3 R_0 V_4|0\rangle = (1 - P_{ab})\Big[-6\langle 0|\mu_0^b R_0 \mu_0^a \mu_0^b \cdot R_0 \mu_0^a \Theta_0^b|0\rangle - 2\sqrt{3}\langle 0|\mu_0^b R_0 \mu_+^a \mu_-^b R_0 \mu_-^a \Theta_+^b|0\rangle\Big]. \tag{A12}$$

The next step involves an application of the Wigner-Eckart Theorem[72]

$$\langle \tau J M|T_k^q|\tau' J' M'\rangle = (-1)^{J-M}\begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix}\langle \tau J\|T_k\|\tau' J'\rangle. \tag{A13}$$

In (A13), T_k^q is the qth component of an irreducible tensor of order k, $\begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix}$ is a Wigner "3j" symbol, and $\langle \tau J\|T_k\|\tau' J'\rangle$

a reduced matrix element which is independent of the quantum numbers M and M'. We will utilize this theorem in an angular reduction which will relate the second term in (A12), which involves nonzero magnetic quantum numbers, to the first. Since R_o is spherically symmetric we will ignore it in this angular reduction. Let us consider the A and B integrations separately and let $\sim$ denote angular equivalence. Since in the Condon and Shortley phase convention[73] $Y_1^m = (-1)^m (Y_1^{-m})^*$ we have

$$\langle 0 | \mu_m^a \mu_{-m}^a | 0 \rangle \sim (-1)^m \langle 1 m | T_0^0 | 1 m \rangle . \tag{A14}$$

Using the Wigner-Eckart theorem gives

$$\langle 0 | \mu_m^a \mu_{-m}^a | 0 \rangle \sim - \begin{pmatrix} 1 & 0 & 1 \\ -m & 0 & m \end{pmatrix} \langle 1 \| T_0 \| 1 \rangle . \tag{A15}$$

Substituting the numerical values[74] for $\begin{pmatrix} 1 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}$ and $\begin{pmatrix} 1 & 0 & 1 \\ \pm 1 & 0 & \mp 1 \end{pmatrix}$ into (A15) shows us that

$$\langle 0 | \mu_+^a \mu_-^a | 0 \rangle = - \langle 0 | \mu_0^a \mu_0^a | 0 \rangle . \tag{A16}$$

Similarly for Atom B

$$\langle 0 | \mu_0^b \mu_{-m}^b \Theta_m^b | 0 \rangle \sim (-1)^m \langle 1 m | T_1^0 | 2 m \rangle . \tag{A17}$$

Using (A13)

$$\langle 0 | \mu_0^b \mu_{-m}^b \Theta_m^b | 0 \rangle \sim \begin{pmatrix} 1 & 1 & 2 \\ -m & 0 & m \end{pmatrix} \langle 1 \| T_1 \| 2 \rangle . \tag{A18}$$

and inserting the numerical values of the "3j" symbols gives us

$$\langle 0|\mu_0^b \mu_-^b \Theta_+^b|0\rangle = -\frac{\sqrt{3}}{2}\langle 0|\mu_0^b \mu_0^b \Theta_0^b|0\rangle . \tag{A19}$$

Substituting (A16) and (A19) into $\langle 0|\mu_0^b R_0 \mu_+^a \mu_-^b R_0 \mu_-^a \Theta_+^b|0\rangle$ in (A12) gives

$$\langle 0|\mu R_0 V_3 R_0 V_4|0\rangle = -9(1-P_{ab})\langle 0|\mu_0^b R_0 \mu_0^a \mu_0^b R_0 \mu_0^a \Theta_0^b|0\rangle . \tag{A20}$$

The reduction proceeds analogously for $\langle 0|\mu R_0 V_4 R_0 V_3|0\rangle$ and $\langle 0|V_3 R_0 \mu R_0 V_4|0\rangle$. For simplicity we can drop the m = o subscripts on μ and Θ. The reduced expression for D_7 now is

$$D_7 = 18(1-P_{ab})\left[\langle 0|\mu^a R_0 \mu^a \mu^b R_0 \mu^b \Theta^a|0\rangle + \langle 0|\mu^a R_0 \mu^b \Theta^a R_0 \mu^a \mu^b|0\rangle + \langle 0|\mu^a \mu^b R_0 \mu^a R_0 \mu^b \Theta^a|0\rangle\right] . \tag{A21}$$

We now substitute equation (A3) for the resolvent into (A21). If we note that from (13) and (16)

$$R_0^A(\omega)|A_0\rangle = R_0^B(\omega)|B_0\rangle = 0 \tag{A22}$$

and

$$R_0^{AB}|A_0\rangle = R_0^{AB}|B_0\rangle = 0 \tag{A23}$$

we find that (A21) becomes

$$D_7 = 18(1-P_{ab})\left[\langle A_0B_0|\mu^a R_0^A \mu^a \mu^b R_0^{AB} \mu^b \Theta^a|A_0B_0\rangle + \langle A_0B_0|\mu^a R_0^A \mu^b \Theta^a R_0^{AB} \mu^a \mu^b|A_0B_0\rangle + \langle A_0B_0|\mu^a \mu^b R_0^{AB} \mu^a R_0^{AB} \mu^b \Theta^a|A_0B_0\rangle\right] . \tag{A24}$$

Using the identity of equation (14) in expression (16) for R_o^{AB} we have

$$R_o^{AB} = -\int_{-\infty}^{\infty} \frac{d\omega}{\pi} \left[\sum_{k \neq 0} \frac{(E_k^A - E_o^A)|A_k\rangle\langle A_k|}{(E_k^A - E_o^A)^2 + \omega^2} \right] \left[\sum_{\ell \neq 0} \frac{(E_\ell^B - E_o^B)|B_\ell\rangle\langle B_\ell|}{(E_\ell^B - E_o^B)^2 + \omega^2} \right] . \tag{A25}$$

Substituting (13) into this gives

$$R_o^{AB} = -\int_{-\infty}^{\infty} \frac{d\omega}{\pi} R_o^A(\omega) R_o^B(\omega) . \tag{A26}$$

If we then substitute (A26) into (A24) we obtain an expression for D_7 in terms of a single and a double integral over frequencies.

$$D_7 = -18(1-P_{ab}) \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \Big\{ \Big[\langle A_o|\mu^a R_o^A \mu^a R_o^A(\omega) \textcircled{H}^a |A_o\rangle \quad +$$

$$\langle A_o|\mu^a R_o^A \textcircled{H}^a R_o^A(\omega) \mu^a |A_o\rangle \Big] \langle B_o|\mu^b R_o^B(\omega) \mu^b |B_o\rangle \Big\} + 18(1-P_{ab})$$

$$\cdot \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{du\,dv}{\pi^2} \Big[\langle A_o|\mu^a R_o^A(u) \mu^a R_o^A(v) \textcircled{H}^a |A_o\rangle \langle B_o|\mu^b R_o^B(u) R_o^B(v) \mu^b |B_o\rangle \Big] . \tag{A27}$$

If we define α , γ , T , and L as in (20) to (23) the final expression for D_7 is

$$D_7 = 9(1-P_{ab}) \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \alpha_A(i\omega) \gamma_B(\omega)$$

$$+ 9(1-P_{ab}) \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{du\,dv}{\pi^2} L_A(u,v) T_B(u,v) \tag{A28}$$

B. Choice of g^{I} and g^{II}

The constants g^{I} and g^{II} are approximations to the frequency-dependent values $\gamma(\omega)/\alpha(i\omega)$ and $\Gamma(u,v)/L(u,v)$. The three methods mentioned for evaluating these are for zero frequency, in the limit as the frequency approaches infinity, or as frequency averages.

1. Zero Frequency

For this case we take the constants to be the ratios with all frequencies equal to zero,

$$g^{I} = \frac{\langle 0|\mu R_0 \Theta R_0 \mu + \mu R_0 \mu R_0 \Theta|0\rangle}{2\langle 0|\mu R_0 \mu|0\rangle} \tag{B1}$$

and

$$g^{II} = -\frac{\langle 0|\mu R_0 \mu R_0 \Theta|0\rangle}{2\langle 0|\mu R_0 R_0 \mu|0\rangle} . \tag{B2}$$

In this approximation we need the first order wavefuntions $R_0\mu\Psi_0$ and $R_0\Theta\Psi_0$. These are known exactly for one-electron systems[58] but not for larger ones and thus (B1) and (B2) shouldn't be too easy to calculate.

2. Infinite Frequency Limit

In the limit of infinite frequency

$$\lim_{\omega\to\infty} R_0(\omega) = \frac{E_0 - H_0}{\omega^2} . \tag{B3}$$

If we set the constants equal to the ratios with this limiting value of $R_o(w)$ we obtain[75]

$$g^{I} = \frac{\langle 0|\mu R_o \Theta [\mu, H_o] + \mu R_o \mu [\Theta, H_o]|0\rangle}{2\langle 0|\mu [\mu, H_o]|0\rangle} \tag{B4}$$

$$g^{II} = -\frac{\langle 0|[H_o, \mu]\mu [\Theta, H_o]|0\rangle}{2\langle 0|[H_o, \mu][\mu, H_o]|0\rangle} . \tag{B5}$$

Expressions (B4) and (B5) may be easier to evaluate than the zero-frequency values since they involve only one resolvent. However the infinite frequency g^{I} and g^{II} shouldn't be as good as the zero frequency ones since the weighting factors in (30) and the analogous integral for D_7^{II} go as ω^{-4} and ω^{-8} respectively as $\omega \to \infty$ and are maximums at w = o.

3. Frequency Averages

A method which seems to be a good compromise between the first two is to replace $R_o(w)$ by its "frequency average"

$$\overline{R_o} = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} R_o(\omega) = |0\rangle\langle 0| - 1 . \tag{B6}$$

This yields the following expressions for g^{I} and g^{II}

$$g^{I} = \frac{\langle 0|\mu R_o \mu \Theta|0\rangle}{\langle 0|\mu^2|0\rangle} \tag{B7}$$

$$g^{II} = -\frac{\langle 0|\mu^2 \Theta|0\rangle}{2\langle 0|\mu^2|0\rangle} . \tag{B8}$$

This choice requires expectation values which should be easier to calculate than those occuring in the other two methods.

For g^{II}, different combinations of the above three are also possible (e.g. one frequency zero and the other in the infinite limit). Exact values of g^{I} and g^{II} have been calculated previously[75] for hydrogen for these various combinations and are quoted below.

$$
\begin{aligned}
g^{I}(0) &= 8.58 \\
\bar{g}^{I} &= 8.25 \\
g^{I}(\infty) &= 7.50
\end{aligned}
\tag{B9}
$$

$g^{II}(u,v)$

$u \backslash v$	0	—	∞
0	1.36	1.83	2.5
—	1.11	1.5	2
∞	0.75	1	1.2

(B10)

As can be seen, neither g^{I} nor g^{II} is actually a constant.

We have chosen the frequency-averaged values, (B7) and (B8), mainly because of their computational convenience. To test this choice D_7 has been calculated for the model system of Section 4 using these two and also the pairs in which the frequencies are zero, (B1) and (B2), and infinite, (B4) and (B5). They are compared with accurate values in Table 21. The accurate values of C_6^{AB} and C_{AB}^{II} given in Table 1 were used in these calculations.

After comparing them we see that the zero and average frequency methods give almost equally good values of D_7 (the zero frequency values average 1.3% difference from the accurate ones and the average frequency 1.6%). The infinite limit values of D_7 are much worse, differing from the accurate ones by about 11%. Thus the average frequency choice seems justified. The slight difference between this and the zero frequency method does not warrant doing the more difficult integrals involved in the latter.

C. D_7 for H-H Using Hirschfelder-Eliason Densities

Hirschfelder and Eliason[76] have calculated C_6 for the interaction of two hydrogen atoms using the electrostatic Hellmann-Feynman Theorem. They consider the long range dispersion force

$$F = \int \left(\frac{Z_1}{r_1^3}\right) \rho_1 \, d\tau_1 \tag{C1}$$

where ρ_1 is the total electronic charge density

$$\begin{aligned} \rho_1 &= \int \Psi^* \Psi \, d\tau_2 \\ &\equiv \langle \Psi | \Psi \rangle_2 \quad . \end{aligned} \tag{C2}$$

The total wavefunction Ψ is not antisymmetrized since overlap is neglected at long range. In terms of the perturbation expansion (3) this density is (neglecting terms which vanish)

$$\begin{aligned} \rho_1 = {} & \langle \Psi_0 | \Psi_0 \rangle_2 + \langle \Psi_0 V R_0 | R_0 V \Psi_0 \rangle_2 \\ & + 2 \langle \Psi_0 | R_0 V R_0 V \Psi_0 \rangle_2 + \cdots \quad . \end{aligned} \tag{C3}$$

If we substitute the expansion $V = \frac{V_3}{R^3} + \frac{V_4}{R^4} + \ldots$ into (C3) we obtain

$$\begin{aligned} \rho_1 = {} & \rho_{00}^{(0)} + R^{-6} \left[\rho_{33}^{(1)} + \rho_{33}^{(2)} \right] \\ & + R^{-7} \left[\rho_{34}^{(1)} + \rho_{34}^{(2)} \right] + \cdots \end{aligned} \tag{C4}$$

where

$$\rho_{00}^{(0)} = \langle \Psi_0 | \Psi_0 \rangle_2 \tag{C5}$$

$$\rho_{33}^{(1)} = \langle \Psi_0 V_3 R_0 | R_0 V_3 \Psi_0 \rangle_2 \tag{C6}$$

$$\rho_{33}^{(2)} = 2 \langle \Psi_0 | R_0 V_3 R_0 V_3 \Psi_0 \rangle_2 \tag{C7}$$

$$\rho_{34}^{(1)} = 2 \langle \Psi_0 V_3 R_0 | R_0 V_4 \Psi_0 \rangle_2 \tag{C8}$$

$$\rho_{34}^{(2)} = 2 \left[\langle \Psi_0 | R_0 V_3 R_0 V_4 \Psi_0 \rangle_2 + \langle \Psi_0 | R_0 V_4 R_0 V_3 | \Psi_0 \rangle_2 \right]. \tag{C9}$$

The first three do not contribute to (C1) since they are even in z. The last two, $\rho_{34}^{(1)}$ and $\rho_{34}^{(2)}$, do and are quoted by Hirschfelder and Eliason.

Let us define a "one-way" value of D_7 with μ_0^a rather than $\mu_0^a + \mu_0^b$

$$\vec{D}_7 = 2 \langle 0 | \mu_0^a R_0 V_3 R_0 V_4 + \mu_0^a R_0 V_4 R_0 V_3 + V_3 R_0 \mu_0^a R_0 V_4 | 0 \rangle \tag{C10}$$

where $\mu_0^a = -z_1$ for an H atom (c.f. equation (11)). Observing (C8) and (C9) we see that D_7 can be expressed as

$$\vec{D}_7 = -\int z_1 \rho_1 \, d\tau_1 . \tag{C11}$$

Furthermore, if we were to reduce (C8) and (C9) as in Appendix A we would find that

$$\vec{D}_7^{I} = -\int z_1 \rho_{34}^{(2)} \, d\tau_1 \tag{C12}$$

and

$$\vec{D}_7^{II} = -\int z_1 \rho_{34}^{(1)} d\tau_1 \ . \tag{C13}$$

We have calculated $\vec{D}_7^{I}$ and $\vec{D}_7^{II}$ with the densities $\rho_{34}^{(2)}$ and $\rho_{34}^{(1)}$. The densities can be expressed as

$$\rho_{34}^{(\ell)} = \sqrt{\frac{3}{4\pi}}\, Y_1^0(\Omega)\, e^{-2r} \sum_{k=1}^{8} \frac{C_k^{(\ell)}}{k!} (2r)^k + Y_3^0 \text{ component.} \tag{C14}$$

The coefficients $C_k^{(1)}$ and $C_k^{(2)}$ are in Table 22.

The Hirschfelder-Eliason density values of $\vec{D}_7^{I}$ and $\vec{D}_7^{II}$ for hydrogen-hydrogen are compared with those from Section 4 in the table below.

	D_7^{I}	D_7^{II}	D_7
Section 4	330.505	64.006	394.511
Densities	330.512	64.007	394.519

(C15)

The agreement is excellent.

D. Checks for the Hydrogen Basis

Although our approximations agree quite well with the accurate value of D_7 we need to verify the accuracy of the latter calculations. This has partially been accomplished in Appendix C. However we still need to check the completeness of our finite basis set.

1. Long-Range Energy Coefficients

First, we can compare the values of C_6^{HH} (Table 1) and C_8^{HH} computed using our basis set with the most accurate values of Kolos[77]. We get

$$C_6^{HH} = 6.499027$$

$$C_8^{HH} = 124.3991$$

which are in exact agreement with those of Kolos[77].

2. Expectation Values Involving R_0

Using (50) we can write

$$\langle 0|\mu R_0 \mu|0\rangle \approx -\sum_{k=1}^{n} \frac{\mu_{0k}^2}{\Delta\epsilon_k} \tag{D1}$$

$$\langle 0|\Theta R_0 \Theta|0\rangle \approx -\sum_{k=1}^{n} \frac{\Theta_{0k}^2}{\Delta\epsilon_k} \tag{D2}$$

$$\langle 0|\mu R_0 \mu \Theta|0\rangle \approx -\sum_{k=1}^{n}\sum_{\ell=1}^{n} \frac{\mu_{0k}\,\mu_{k\ell}\,\Theta_{\ell 0}}{\Delta\epsilon_k} \tag{D3}$$

$$\langle 0|\mu R_0 \Theta \mu|0\rangle \approx -\sum_{k=1}^{n}\sum_{\ell=1}^{n} \frac{\mu_{0k}\,\Theta_{k\ell}\,\mu_{\ell 0}}{\Delta\epsilon_k} \tag{D4}$$

$$\langle 0|\mu R_0 \mu R_0 \Theta|0\rangle \approx \sum_{k=1}^{n}\sum_{\ell=1}^{n} \frac{\mu_{0k}\mu_{k\ell}\Theta_{\ell 0}}{\Delta\epsilon_k \Delta\epsilon_\ell} \quad . \tag{D5}$$

All of the left hand quantities can be evaluated exactly using the known[58] first order wavefunctions $R_0\mu\Psi_0$ and $R_0\Theta\Psi_0$. The agreement with the approximations is given in the following table.

Equation	Exact	Approximation
D1	- 2.25	- 2.25000000
D2	- 7.50	- 7.50000000
D3	8.25	8.24999994
D4	8.25	8.24999993
D5	- 14.625	- 14.6249999

(D6)

Since our basis set contains both $\mu\Psi_0$ and $\Theta\Psi_0$, relations of the following kind should be satisfied exactly[78].

$$\langle 0|\mu^2|0\rangle = -\sum_{k=1}^{n} \mu_{0k}^2 \tag{D7}$$

$$\langle 0|\mu^2\Theta|0\rangle = -\sum_{k=1}^{n}\sum_{\ell=1}^{n} \mu_{0k}\mu_{k\ell}\Theta_{\ell 0} \tag{D8}$$

$$N_e = 2\sum_{k=1}^{n} \Delta\epsilon_k \mu_{0k}^2 \tag{D9}$$

$$2N_e\langle 0|r_i^2|0\rangle = 2\sum_{k=1}^{n} \Delta\epsilon_k \Theta_{0k}^2 \quad . \tag{D10}$$

This was found to be true for the number of significant figures (9) carried in the computation.

E. Calculation of Two-Term $\bar{\gamma}$

From equation (57) we have

$$\tilde{\Psi}^{(1)} = \sqrt{\frac{4\pi}{3}} \sum_{\lambda=1}^{N_e} (c_1 r_\lambda + c_2 r_\lambda^2) Y_1^0(\hat{r}_\lambda) \Psi_0 \ . \tag{E1}$$

Using equation (A8) and dropping the subscript give us

$$\mu = -\sqrt{\frac{4\pi}{3}} \sum_{\lambda=1}^{N_e} r_\lambda Y_1^0(\hat{r}_\lambda) \ . \tag{E2}$$

We also define

$$\eta = -\sqrt{\frac{4\pi}{3}} \sum_{\lambda=1}^{N_e} r_\lambda^2 Y_1^0(\hat{r}_\lambda) \ . \tag{E3}$$

Then in terms of these symbols

$$\tilde{\Psi}^{(1)} = -(c_1\mu + c_2\eta)\Psi_0 \ . \tag{E4}$$

Since from equation (59) the two-term approximation for $\bar{\gamma}$ is

$$\bar{\gamma} \approx 2 \langle \tilde{\Psi}^{(1)} | \mu \Theta | \Psi_0 \rangle \tag{E5}$$

if we substitute (E4) into (E5) we obtain $\bar{\gamma}$ in terms of μ and η .

$$\bar{\gamma} \approx -2 \left[c_1 \langle 0 | \mu^2 \Theta | 0 \rangle + c_2 \langle 0 | \eta \mu \Theta | 0 \rangle \right] . \tag{E6}$$

Similarly the two-term approximation to the polarizability is

$$\alpha \approx 2 \left[c_1 \langle 0 | \mu^2 | 0 \rangle + c_2 \langle 0 | \mu \eta | 0 \rangle \right] . \tag{E7}$$

We determine the constants C_1 and C_2 by extremizing the Hylleraas-type functional

$$J = \langle \tilde{\Psi}^{(1)} | H_0 - E_0 | \tilde{\Psi}^{(1)} \rangle + 2 \langle \tilde{\Psi}^{(1)} | \mu | \Psi_0 \rangle \tag{E8}$$

with respect to variations in C_1 and C_2. If we define

$$H_{11} = \langle 0 | \mu (H_0 - E_0) \mu | 0 \rangle \tag{E9}$$

$$H_{22} = \langle 0 | \eta (H_0 - E_0) \eta | 0 \rangle \tag{E10}$$

$$H_{12} = H_{21} = \langle 0 | \mu (H_0 - E_0) \eta | 0 \rangle \tag{E11}$$

$$S_{11} = \langle 0 | \mu^2 | 0 \rangle \tag{E12}$$

$$S_{12} = \langle 0 | \mu \eta | 0 \rangle \tag{E13}$$

the formulas for C_1 and C_2 are

$$C_1 = \frac{H_{22} S_{11} - S_{12} H_{12}}{H_{11} H_{22} - H_{12}^2} \tag{E14}$$

$$C_2 = \frac{H_{11} S_{12} - S_{11} H_{12}}{H_{11} H_{22} - H_{12}^2} \, . \tag{E15}$$

Substituting these values (E14) and (E15) into (E6) gives the two-term expression for $\overline{\gamma}$.

Practically, one other approximation has also been made. We have assumed that if f and g are two functions then

$$\langle 0 | f(H_0 - E_0) g | 0 \rangle = \frac{1}{2} \sum_{\lambda=1}^{N_e} \langle 0 | \nabla_\lambda f \cdot \nabla_\lambda g | 0 \rangle . \tag{E16}$$

This substitution is strictly true only if Ψ_0 is the exact zeroth order wavefunction but is commonly used[54,63] and simplifies the calculations immensely. If we make this substitution in (E9) - (E11) we obtain

$$H_{11} = \frac{1}{2} N_e \tag{E17}$$

$$H_{12} = H_{21} = \frac{2}{3} N_e \langle 0 | r_1 | 0 \rangle \tag{E18}$$

$$H_{22} = N_e \langle 0 | r_1^2 | 0 \rangle \tag{E19}$$

where N_e is the number of electrons. If we let $\langle \ \rangle$ signify a ground-state expectation value the expressions for C_1 and C_2 used in our approximation are

$$C_1 = \frac{6}{N_e} \left[\frac{3 \langle r_1^2 X_\mu^2 \rangle - 2 \langle r_1 X_\eta \mu \rangle}{9 \langle r_1^2 \rangle - 8 \langle r_1 \rangle^2} \right] \tag{E20}$$

$$C_2 = \frac{3}{N_e} \left[\frac{3 \langle \eta \mu \rangle - 4 \langle r_1 X_\mu^2 \rangle}{9 \langle r_1^2 \rangle - 8 \langle r_1 \rangle^2} \right] \tag{E21}$$

F. Helium Atom Calculation

In this appendix we will give a short description of the helium calculation.

For the accurate computations involving the helium atom we have used a basis set $\Psi_{n\ell m} = F_{n\ell m}\Psi_0$ where

$$F_{n\ell m} = \sum_{\lambda=1}^{2} r_\lambda^n Y_\ell^m(\hat{r}_\lambda) \qquad n \geq \ell \tag{F1}$$

and Ψ_0 is the 20-term Hart-Herzberg[64] ground state wavefunction of the form

$$\Psi_0 = \mathcal{N}\sum_{i=1}^{20} a_i e^{-\frac{1}{2}\kappa s} s^{\ell_i} t^{2m_i} u^{n_i} . \tag{F2}$$

In (F2) the variables are

$$s = r_1 + r_2 \qquad t = r_1 - r_2 \qquad u = r_{12} . \tag{F3}$$

As in the previous Appendix we make the substitution in the Hamiltonian matrix.

$$\langle \Psi_{k\ell m} | H_0 - E_0 | \Psi_{k'\ell' m'} \rangle \approx \frac{1}{2}\sum_{\lambda=1}^{2} \langle \Psi_0^2 | \nabla_\lambda F_{k\ell m} \cdot \nabla_\lambda F_{k'\ell' m'} \rangle . \tag{F4}$$

Then all the necessary integrals can be expressed in terms of the set of basic integrals

$$I_\lambda^{kk'} = \langle \Psi_0 | r_1^{k+\lambda-1} r_2^{k'+\lambda-1} Y_\lambda^0(1) Y_\lambda^0(2) | \Psi_0 \rangle . \tag{F5}$$

To evaluate these substitute (F2) into (F4) and expand s and t using

$$(r_1 \pm r_2)^n = \sum_{k=0}^{n} \binom{n}{k} (\pm 1)^k r_1^{n-k} r_2^k \quad . \tag{F6}$$

Then $I_\lambda^{kk'}$ is

$$I_\lambda^{kk'} = \eta^2 \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \sum_{k=0}^{l_i+l_j} \sum_{k'=0}^{\lambda m_i+\lambda m_j} a_i a_j \binom{l_i+l_j}{k} \binom{\lambda m_i+\lambda m_j}{k'} (-1)^{k'} J_{ij\lambda}^{kk'kk'} \tag{F7}$$

where

$$J_{ij\lambda}^{kk'kk'} = \iint e^{-\lambda\eta(r_1+r_2)} r_1^{\alpha} r_2^{\beta} r_{12}^{\gamma} Y_\lambda^0(1) Y_\lambda^0(2) \, d\tau_1 d\tau_2 \tag{F8}$$

and

$$\alpha = l_i + l_j + \lambda m_i + \lambda m_j + k + \lambda - k - k' - 1 \tag{F9}$$

$$\beta = k + k' + k' + \lambda - 1 \tag{F10}$$

$$\gamma = n_i + n_j . \tag{F11}$$

Calais and Löwdin[79] have given a simple method of evaluating integrals of the form

$$J_{l\lambda}^{m\mu} = \iint f(r_1) g(r_2) h(r_{12}) Y_l^m(1) Y_\lambda^\mu(2) \, d\tau_1 d\tau_2 . \tag{F12}$$

This method can be used for $J_{ij\lambda}^{kk'kk'}$. Summing (F7) finally gives the basic integrals $I_\lambda^{kk'}$.

Having evaluated these integrals and the Hamiltonian and overlap matrix elements it is a simple matter to first orthonormalize the

basis set and then to diagonalize the Hamiltonian matrix in the orthonormal basis. One slight complicating factor encountered was the loss of accuracy in the orthonormalization step when large basis sets were used. A Schmidt orthogonalization subroutine based on a method from Morse and Feshbach[93] was found to give better results then an alternate method in which the overlap matrix was diagonalized using the University of Wisconsin Computing Center Library Subroutine for the CDC 3600. For six-membered basis sets the following table lists the worst diagonal and off-diagonal elements of the overlap matrix after orthonormalization.

l	diagonal	off-diagonal
1	$9.99998927 \times 10^{-1}$	$7.62846321 \times 10^{-6}$
2	$9.99999901 \times 10^{-1}$	$4.69759107 \times 10^{-5}$

(F13)

These became progessively worse as the basis size was increased.

G. Checks for Helium Basis

Just as for the hydrogen basis, we need verification of the adequacy of the basis set used for helium.

1. Long-Range Energy Coefficients

Values of C_6 and C_8 obtained with our helium and hydrogen basis are compared with what are probably the most accurate values below (in parentheses)

$$C_6^{HeH} = 2.816 \quad (2.83^{80,81}) \tag{G1}$$

$$C_6^{HeHe} = 1.458 \quad (1.47^{80,81},\ 1.4605 \pm .0025^{82}) \tag{G2}$$

$$C_8^{HeH} = 41.73 \quad (41.9^{80}) \tag{G3}$$

$$C_8^{HeHe} = 14.06 \quad (14.2^{80}) \tag{G4}$$

These also compare well with other literature values[83].

2. Polarizabilities

The static dipole and quadrupole polarizabilities are compared below with what are probably the most accurate values (atomic units)

$$\alpha_d = 1.379 \quad (1.384^{84},\ 1.380^{80}) \tag{G5}$$

$$\alpha_q = 2.430 \quad (2.440^{80}) \tag{G6}$$

3. Sum Rules

The dipole and quadrupole sum rules for S_o have also been checked. There are, as in Appendix D,

$$N_e = 2 \sum_{k=1}^{N} \Delta \epsilon_k \mu_{ok}^2 \tag{G7}$$

$$2N_e \langle o | r_1^2 | o \rangle = 2 \sum_{k=1}^{N} \Delta \epsilon_k \Theta_{ok}^2 . \tag{G8}$$

Unlike in Appendix D we would not necessarily expect (G8) to be satisfied exactly since the matrix elements μ_{ok} and Θ_{ok} do not contain the exact zeroth order wavefunction. In the table below we have compared the summation values with N_e and with $\langle o | r_1^2 | o \rangle$ from Pekeris[91] and from the Hart-Herzberg ground-state wavefunctions.

Equation	Summation	Accurate	Hart-Herzberg
G7	2.000000	2	
G8	4.773296	4.773932[(a)]	4.773321

(G9)

(a) Pekeris. See Reference 91.

Comparing the summation value for (G8) with the Pekeris and Hart-Herzberg values we see that the summation is accurate to four figures. The difference is due more to the inaccuracy of the approximate ground state wavefunction rather than to the fact that the basis set is not complete (since the agreement with the Hart-Herzberg $\langle o | r_1^2 | o \rangle$ is to six figures).

H. Properties of Hydrogen and Helium Basis Sets

Let $\phi_{n\ell m}$ be an orthonormal basis set

$$\phi_{n\ell m} = \sum_{k=1}^{N} c_k F_{k\ell m} \Psi_0 \tag{H1}$$

such that, if H_0 and E_0 are the Hamiltonian and ground-state energy of the atom under consideration,

$$\langle \phi_{n\ell m} | H_0 - E_0 | \phi_{n'\ell' m'} \rangle = \Delta\epsilon_n^{\ell} \, \delta_{nn'} \, \delta_{\ell\ell'} \, \delta_{mm'} \, . \tag{H2}$$

The energy $\Delta\epsilon_n^{\ell}$ is an effective transition energy for the atom. We also define the effective oscillator strengths

$$f_{n0}^{1} = 2\Delta\epsilon_n^{1} \, |\langle \phi_{n10} | \mu | \Psi_0 \rangle|^2 \tag{H3}$$

$$f_{n0}^{2} = 2\Delta\epsilon_n^{2} \, |\langle \phi_{n20} | \Theta | \Psi_0 \rangle|^2 \, . \tag{H4}$$

1. Hydrogen

For the hydrogen atom we have used a ten-membered set $\{\phi_{n10}\}$ and a twenty-membered set $\{\phi_{n20}\}$. The $\phi_{n\ell m}$ are chosen to be linear combinations of the orthonormal Löwdin-Shull[56,57] orbitals (which are themselves linear combinations of functions of the type $F_{nlm} \Psi_0$).

The effective transition energies and oscillator strengths for the dipole and quadrupole transitions in hydrogen are listed in Table 23. It should be noted that $\Delta\epsilon_1^1$ and $\Delta\epsilon_1^2$ are upper bounds to the first dipole and quadrupole transition energies which are 0.375 and

0.444 .... respectively. Also as in (D9) and (D10) we find that the sums of f_{ko}^{1} and f_{ko}^{2} are 1.00000000 and 6.00000000 respectively.

2. Helium

For helium we have used a six-membered basis $\{\phi_{n10}\}$ and a six-membered $\{\phi_{n20}\}$. The zeroth order wavefunction is the twenty-term ground-state wavefunction of Hart and Herzberg[64].

The effective transition energies and oscillator strengths for dipole and quadrupole transitions in helium are listed in Table 24. The oscillator strength sums (G7) and (G8) are 2.000000 and 4.773296. An accurate value of the latter is given in (G9).

Table 1

Accurate and Approximate Values of C_6 and C^{II} for H_ζ-H (atomic units)

		C^{II}		
ζ	C_6	Accurate	(47)	(48)
1.0	6.499027	4.932417	5.0625	4.8743
1.1	4.862103	3.340541	3.4265	3.3001
1.2	3.703157	2.306445	2.3620	2.2765
1.3	2.865143	1.620665	1.6559	1.5977
1.4	2.247960	1.157293	1.1792	1.1392
1.5	1.785978	0.8387895	0.85207	0.82430
1.6	1.435108	0.6163758	0.62414	0.60468
1.7	1.165113	0.4587684	0.46305	0.44927
1.8	0.9548598	0.3455498	0.34765	0.33780
1.9	0.7893366	0.2631760	0.26395	0.25684
2.0	0.6577167	0.2025257	0.20250	0.19732

Table 2

Comparison of Accurate and Approximate Values of D_7^I and D_7^{II} for H_ζ-H (atomic units)

	D_7^I		D_7^{II}	
ζ	Accurate	Eq. (31)	Accurate	Eq. (32)
1.0	0	0	0	0
1.1	77.74	76.29	7.91	7.83
1.2	96.68	94.91	9.61	9.51
1.3	93.84	92.17	9.02	8.93
1.4	83.76	82.31	7.73	7.65
1.5	72.14	70.94	6.35	6.29
1.6	61.18	60.20	5.12	5.07
1.7	51.56	50.77	4.09	4.05
1.8	43.40	42.76	3.25	3.23
1.9	36.58	36.07	2.59	2.57
2.0	30.93	30.52	2.07	2.05

Table 3

Comparison of Accurate and Approximate Values of D_7 for H_ζ-H (atomic units)

ζ	Accurate	Approx. (31 and 32)	Unsöld (26)
1.0	0	0	0
1.1	85.65	84.12	72.84
1.2	106.29	104.42	90.31
1.3	102.87	101.10	87.29
1.4	91.48	89.96	77.51
1.5	78.49	77.23	66.39
1.6	66.29	65.27	55.97
1.7	55.64	54.82	46.90
1.8	46.65	45.99	39.25
1.9	39.17	38.64	32.91
2.0	33.00	32.57	27.68

Table 4

Polarizabilities for Rare Gas Atoms[a]

Atom	Two-Term[b]	UHF[c]	Experimental[d]
He	1.49	1.48	1.384
Ne	2.66	2.82	2.67
Ar	13.4	16.5	11.1
Kr	21.0		16.7

(a) All values in atomic units

(b) Zeroth order wavefunctions are Clementi's analytical Hartree-Fock. See Reference 62

(c) Langhoff and Hurst. See Reference 61

(d) Dalgarno and Kingston. See Reference 84

Table 5

Comparison of Accurate and Approximate Values of $\bar{\gamma}$ and g^{I} for Helium[a]

	Accurate (Approx. 1)	Two-Term (Approx. 2)	Unsöld (Approx. 3)
$\bar{\gamma}$	2.396	2.391	1.815
g^{I}	1.592	1.588	1.206

(a) all values in atomic units

Table 6

D_7 Coefficients for $He^- - H^+$ (Atomic Units)

Calculation	D_7^I	D_7^{II}	D_7	%[a]
Accurate	111	8.6	120	0
Approx. 1	112	9.6	122	1.8
Approx. 2	112	9.6	122	1.8
Approx. 3	119	9.6	129	7.2
Approx. 4	98.1	9.8	108	10.2

(a) $\% = \dfrac{D_7 - D_7 \text{ (accurate)}}{D_7 \text{ (accurate)}}$

Table 7

$\vec{D}_7$ Coefficients for He-He (Atomic Units)

Calculation	$\vec{D}_7^{I}$	$\vec{D}_7^{II}$	$\vec{D}_7$	%(a)
Accurate	15.5	2.9	18.4	0
Approx. 1	13.9	2.7	16.6	9.6
Approx. 2	13.9	2.7	16.6	9.6
Approx. 3	10.6	2.7	13.2	28.0
Approx. 4	11.3	2.8	14.1	23.1

(a) $\% = \dfrac{\vec{D}_7 - \vec{D}_7 \text{ (accurate)}}{\vec{D}_7 \text{ (accurate)}}$

Table 8

C^{II}_{AB} Interpolation Coefficients

i/j	2	3	4	5	6
2	0.53584684	- 2.0233039	3.2221947	- 2.4456768	0.72374932
3	- 2.0233039	16.679168	- 33.172501	28.548756	- 9.1951487
4	3.2221947	- 33.172501	72.976717	- 66.230501	22.016869
5	- 2.4456768	28.548756	- 66.230501	61.879779	- 20.934658
6	0.72374932	- 9.1951487	22.016869	- 20.934658	7.1589284

Table 9

Sum Rules for Hydrogen and Rare Gas Atoms (Atomic Units)

Atom	S(-2)	S(-3)	S(-4)	S(-5)	S(-6)
H[a]	4.5	10.75	26.583333	67.173610	172.188079
He[b]	1.379	1.403	1.520	1.712	1.982
He[c]	1.384	1.425	1.561	1.775	2.066
Ne[d]	2.680	2.545	2.877	3.641	4.984
Ar[d]	11.08	16.52	26.90	46.85	86.34
Kr[d]	16.79	28.77	54.69	111.1	237.6

(a) Exact. Reference 49

(b) Calculated with Hart-Herzberg φ_0 . See Section 8

(c) S(-2) from Reference 84. S(-4) and S(-6) from Reference 67. S(-3) and S(-5) interpolated.

(d) S(-2), S(-4), and S(-6) from Reference 67. S(-3) and S(-5) interpolated.

Table 10

Comparison of Sum Rule Interpolated and Variation-Perturbation C_{AB}^{II}

Diatom	C_{AB}^{II} (sum rules)	C_{AB}^{II} (var. - pert.)
H-H	4.932447	4.932417
He-H	1.268	1.267
He-He	0.4550	0.4542

Table 11

Sum Rule Interpolated C_{AB}^{II} (atomic units)

	H	He	Ne	Ar	Kr
H	4.93	1.28	2.30	11.3	17.4
He		0.458	0.851	3.54	5.19
Ne			1.60	6.50	9.51
Ar				29.0	43.3
Kr					65.2

Table 12

Rare Gas Expectation Values $\sum_i \langle 0 | r_i^n | 0 \rangle$ (atomic units)

n	He[a]	Ne[b]	Ar[b]	Kr[b]
1	1.859	7.892	16.07	26.24
2	2.387	9.376	26.03	39.52
3	3.934	14.40	55.99	87.94
4	7.937	27.28	144.9	245.1
5	18.96	62.09	437.8	800.6

(a) From Hart-Herzberg wfn. This paper

(b) Fraga and Malli. Reference 69

Table 13

Approximate C_{AB}^{II} from (47) (Atomic Units)

	H	He	Ne	Ar	Kr
H	5.06	1.25	1.62	8.49	12.9
He		0.479	0.820	3.71	5.64
Ne			1.80	7.10	10.8
Ar				30.2	45.9
Kr					69.7

Table 14

Rough Dispersion Dipole Coefficients D_7^{AB} for Diatoms A^-B^+ (atomic units)

A \ B	H	He	Ne	Ar	Kr
H	0	- 122	- 247	- 455	- 424
He		0	- 7.0	191	368
Ne			0	444	825
Ar				0	753
Kr					0

Table 15

Expectation Values $\langle 0|\mu^2|0\rangle$ and $\langle 0|\mu^2 \Theta|0\rangle$ (a)

Atom	$\langle 0\|\mu^2\|0\rangle$	$\frac{1}{3}\sum_i \langle 0\|r_i^2\|0\rangle$	$\langle 0\|\mu^2 \Theta\|0\rangle$	$-\frac{2}{15}\sum_i \langle 0\|r_i^4\|0\rangle$
H(b)	1.0	1.0	- 3.0	- 3.0
He(c)	0.7524	0.7956	- 0.9863	- 1.058
He(d)	0.7899	0.7899	- 1.037	- 1.037
Ne(d)	2.028	3.125	- 2.261	- 3.638
Ar(d)	5.475	8.679	- 10.88	- 19.31
Kr(d)	7.877	13.17	- 17.57	- 32.68

(a) All values in atomic units

(b) Exact

(c) Hart and Herzberg ground state wavefunction. Reference 64

(d) Clementi ground state Hartree-Fock wavefunction. Reference 62

Table 16

Properties of Hydrogen and Rare Gas Atoms[a]

Atom	C_1	C_2	$\bar{\gamma}$	g^I	g^{II}
H[b]			16.50	8.25	1.50
He[c]			2.396	1.59	0.655
He[d]	0.3237	0.3771	2.525	1.60	0.656
Ne[d]	0.0225	0.3640	8.617	2.12	0.558
Ar[d]	0.0097	0.5028	39.21	3.58	0.994
Kr[d]	- 0.1066	0.5600	73.06	4.64	1.12

(a) All values in atomic units

(b) Exact

(c) Hart-Herzberg ground state wavefunctions. Reference 64.

$\bar{\gamma}$ Calculated as in Section 8

(d) Clementi Hartree-Fock ground state wavefunction. Reference 62

Table 17

D_7^I for Diatoms A^-B^+ (atomic units)

A \ B	H	He	Ne	Ar	Kr
H	0	- 112	- 206	- 560	- 629
He		0	9.59	115	238
Ne			0	175	407
Ar				0	577
Kr					0

Table 18

D_7^{II} for Diatoms A^-B^+ (atomic units)

A \ B	H	He	Ne	Ar	Kr
H	0	- 9.63	- 19.5	- 51.5	- 60.2
He		0	- 0.75	10.8	21.5
Ne			0	25.5	47.8
Ar				0	47.5
Kr					0

Table 19

Dispersion Dipole Coefficients D_7^{AB} for Diatoms A^-B^+ (atomic units)

A \ B	H	He	Ne	Ar	Kr
H	0	- 122	- 225	- 612	- 689
He		0	8.84	125	259
Ne			0	200	455
Ar				0	625
Kr					0

Table 20

Comparison of Overlap Dipoles and D_7R^{-7} Contributions to Dispersion Dipole[a]

A^+B^-	R	Overlap ($x10^3$)	D_7R^{-7} ($x10^3$)	Total ($x10^3$)
HeH[b]	3.0		- 54	158
HeH[c]	5.48[h]	2.14	- 0.81	
HeNe[c]	5.03[i]	- 0.171	- 0.109	
HeNe[d]	5.03	- 0.153	- 0.109	
HeAr[c]	5.65[i]	3.23	- 0.68	
HeAr[d]	5.65	3.24	- 0.68	
HeAr[e]	5.65	6.43	- 0.68	
HeAr[f]	5.65	5.61	- 0.68	
HeAr[g]	5.65	4.68	- 0.68	
NeAr[c]	5.82[i]	5.66	- 0.88	
NeAr[d]	5.82	5.68	- 0.88	
NeAr[g]	5.82	7.56	- 0.88	

(a) Atomic units. Multiply by 2.54 to get Debyes

(b) Total dipole from Bender and Davidson. Reference 85

(c) Overlap dipole from Byers Brown and Whisnant. Reference 75

(d) Overlap dipole from Matcha and Nesbet. Reference 35

(e) Overlap dipole from McQuarrie and Bernstein. Reference 39

(f) Overlap dipole from Levine. Reference 40

(g) Overlap dipole from Sears. Reference 38

(h) Collision diameter. Reference 75

(i) Collision diameter. Reference 86

Table 21

Comparison of Approximate D_7 for H_ζ-H Using Different g^I and g^{II}

(atomic units)

ζ	zero[a]	infinite[b]	average[c]	accurate[d]
1.1	86.4	75.6	84.1	85.7
1.2	107.3	93.9	104.4	106.3
1.3	104.0	90.9	101.1	102.9
1.4	92.5	80.9	90.0	91.5
1.5	79.5	69.5	77.2	78.5
1.6	67.2	58.8	65.3	66.3
1.7	56.5	49.4	54.8	55.6
1.8	47.4	41.5	46.0	46.6
1.9	39.8	34.8	38.6	39.2
2.0	33.6	29.4	32.6	33.0

(a) Equations (B1) and (B2)

(b) Equations (B4) and (B5)

(c) Equations (B7) and (B8)

(d) Calculated in Section 4

Table 22

Coefficients in Perturbed Densities[a]

K	$C_k^{(1)}$	$C_k^{(2)}$
1	0	35.233
2	0	17.616
3	1.5673	10.570
4	3.0983	7.0466
5	1.3753	2.5927
6	- 0.76255	- 0.55149
7	0.17083	0.061489
8	- 0.015535	0

(a) See Reference 76

Table 23

Effective Eigenenergies and Oscillator Strengths for Hydrogen

(atomic units)

	Dipole		Quadrupole	
K	$\Delta\varepsilon^1_k$	f^1_{ko}	$\Delta\varepsilon^2_k$	f^2_{ko}
1	0.37500006	0.41619993	0.44444445	0.53393665
2	0.44533064	0.08803654	0.46880284	0.24219681
3	0.48877611	0.08993244	0.48249939	0.21397687
4	0.56134416	0.10723836	0.49971330	0.31121155
5	0.68364018	0.10489786	0.52424651	0.40891305
6	0.89169023	0.08700329	0.55708044	0.49348553
7	1.2698693	0.06013601	0.59980726	0.55611221
8	2.0478339	0.03259492	0.65484807	0.58803528
9	4.0423429	0.01199044	0.72574707	0.58373424
10	12.194172	0.00197021	0.81771087	0.54296444
11			0.93854046	0.47137589
12			1.1002748	0.37959182
13			1.3222208	0.28096802
14			1.6368734	0.18863003
15			2.1023713	0.11262701
16			2.8312742	0.05803830
17			4.0658247	0.02459282
18			6.4118735	0.00787176
19			11.785552	0.00160461
20			29.649342	0.00013317

Table 24

Effective Eigenenergies and Oscillator Strengths for Helium

(atomic units)

	Dipole		Quadrupole	
K	$\Delta \varepsilon^1_k$	f^1_{ko}	$\Delta \varepsilon^2_k$	f^2_{ko}
1	0.787081	0.290484	0.856236	0.170121
2	0.913236	0.348200	1.00739	0.959716
3	1.22217	0.495962	1.31419	1.44022
4	1.89959	0.498469	1.95227	1.37529
5	3.74491	0.302369	3.53727	0.706164
6	11.7497	0.064516	9.28201	0.121785

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