

valid to the fourth power of the perturbation parameter. This expansion is in agreement with the fourth order energy given by Niessen<sup>21</sup>.

Having obtained the necessary expansion for  $E^{(4)}$ , the expectation values of the dipole and quadrupole tensors may be readily obtained. Upon expressing  $H'$  in terms of the dipole and quadrupole moment operators and the field parameters it is found that

$$\begin{aligned}
 E^{(4)} = E_0 &- \langle \mu_\alpha^{(0)} \rangle F_\alpha - \langle \Theta_{\alpha\beta}^{(0)} \rangle F_{\alpha\beta} - \frac{1}{2} \alpha_{\alpha\beta} F_\alpha F_\beta \\
 &- A_{\gamma,\alpha\beta} F_\gamma F_{\alpha\beta} - \frac{1}{2} C_{\alpha\beta,\gamma\delta} F_{\alpha\beta} F_{\gamma\delta} \\
 &- \frac{1}{3} \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - \frac{1}{4} \delta_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta. \quad (105)
 \end{aligned}$$

where all the terms in the third and fourth order summations involving the quadrupole operator have been neglected and the following definitions have been made:

$$E_0 = \langle 0 | H_0 | 0 \rangle \quad (106)$$

$$\langle \mu_\alpha^{(0)} \rangle = \langle 0 | \mu_\alpha | 0 \rangle \quad (107)$$

$$\langle \Theta_{\alpha\beta}^{(0)} \rangle = \langle 0 | \Theta_{\alpha\beta} | 0 \rangle \quad (108)$$

$$\alpha_{\alpha\beta} = 2 \sum_{m \neq 0} \frac{\langle 0 | \mu_\alpha | m \rangle \langle m | \mu_\beta | 0 \rangle}{E_m - E_0} \quad (109)$$

$$A_{\gamma,\alpha\beta} = \sum_{m \neq 0} \frac{\langle 0 | \mu_\gamma | m \rangle \langle m | \Theta_{\alpha\beta} | 0 \rangle}{E_m - E_0} \quad (110)$$

$$C_{\alpha\beta,\gamma\delta} = 2 \sum_{m \neq 0} \frac{\langle 0 | \Theta_{\alpha\beta} | m \rangle \langle m | \Theta_{\gamma\delta} | 0 \rangle}{E_m - E_0} \quad (111)$$

$$\begin{aligned}
 \beta_{\alpha\beta\gamma} = 3 \sum_{\substack{m \neq 0 \\ n \neq 0}} &\frac{\langle 0 | \mu_\alpha | n \rangle \langle n | \mu_\beta | m \rangle \langle m | \mu_\gamma | 0 \rangle}{(E_m - E_0)(E_n - E_0)} \\
 &- 3 \sum_{m \neq 0} \frac{\langle 0 | \mu_\alpha | m \rangle \langle m | \mu_\beta | 0 \rangle \langle 0 | \mu_\gamma | 0 \rangle}{(E_m - E_0)^3} \quad (112)
 \end{aligned}$$

$$\begin{aligned}
\gamma_{\alpha\beta\gamma\delta} = & 4 \sum_{\substack{m \neq 0 \\ n \neq 0 \\ p \neq 0}} \frac{\langle 0 | \mu_\alpha | p \rangle \langle p | \mu_\beta | n \rangle \langle n | \mu_\gamma | m \rangle \langle m | \mu_\delta | 0 \rangle}{(E_m - E_0)(E_n - E_0)(E_p - E_0)} \\
& + 4 \sum_{m \neq 0} \frac{\langle 0 | \mu_\alpha | m \rangle \langle m | \mu_\beta | 0 \rangle \langle 0 | \mu_\gamma | 0 \rangle \langle 0 | \mu_\delta | 0 \rangle}{(E_m - E_0)^2} \\
& - 4 \sum_{\substack{m \neq 0 \\ n \neq 0}} \frac{\langle 0 | \mu_\alpha | n \rangle \langle n | \mu_\beta | 0 \rangle \langle 0 | \mu_\gamma | m \rangle \langle m | \mu_\delta | 0 \rangle}{(E_m - E_0)^2 (E_n - E_0)} \\
& - 8 \sum_{\substack{m \neq 0 \\ n \neq 0}} \frac{\langle 0 | \mu_\alpha | n \rangle \langle n | \mu_\beta | m \rangle \langle m | \mu_\gamma | 0 \rangle \langle 0 | \mu_\delta | 0 \rangle}{(E_m - E_0)^2 (E_n - E_0)} \quad (113)
\end{aligned}$$

The expectation values listed in equations (107) and (112) vanish for atoms since all states are of a definite parity and  $\mu_\alpha$  is of odd parity. The expectation values listed in equations (108) and (110) will vanish for S-states which follows by invoking the Wigner-Eckart Theorem. With the above definitions the electric dipole and quadrupole moment tensors are given by

$$\begin{aligned}
\langle \mu_\alpha^{(3)} \rangle &= -\frac{\partial E^{(4)}}{\partial F_\alpha} \\
&= \langle \mu_\alpha^{(0)} \rangle + \alpha_{\alpha\beta} F_\beta + A_{\gamma,\alpha\beta} F_{\alpha\beta} \\
&\quad + \beta_{\alpha\beta\gamma} F_\beta F_\gamma + \gamma_{\alpha\beta\gamma\delta} F_\beta F_\gamma F_\delta \quad (114)
\end{aligned}$$

and

$$\begin{aligned}
\langle \Theta_{\alpha\beta}^{(3)} \rangle &= -\frac{\partial E^{(4)}}{\partial F_{\alpha\beta}} \\
&= \langle \Theta_{\alpha\beta}^{(0)} \rangle + A_{\gamma,\alpha\beta} F_\gamma + C_{\alpha\beta,\gamma\delta} F_{\gamma\delta} \quad (115)
\end{aligned}$$

where terms in the field gradient  $F_{\alpha\beta}$  have been kept up to only first order. This is the conventional expansion<sup>18</sup> up to some slight nota-

tional differences in the normalization of the  $\beta_{\alpha\beta\gamma}$ ,  $A_{\gamma,\alpha\beta}$ , etc. Note that  $\alpha_{\alpha\beta}$  is the familiar static polarizability and  $\beta_{\alpha\beta\gamma}$  and  $\gamma_{\alpha\beta\gamma\delta}$  are tensors characterizing the quadratic and cubic behavior respectively of the dipole polarizability.  $A_{\gamma,\alpha\beta}$  determines both the dipole induced by a field gradient and the quadrupole induced by a uniform field. Of the above tensors, only two may be evaluated using oscillator strengths, however for S-state atoms these are the dominant contributions.  $\alpha_{\alpha\beta}$  may be evaluated using dipole oscillator strengths and  $C_{\alpha\beta,\gamma\delta}$  may be evaluated using quadrupole oscillator strengths.

Another important interaction where multipole oscillator strengths may be used is the Van der Waals interaction between distant atoms. For the following treatment to be applicable, the atoms must be distant enough such that the overlap of atomic wavefunctions is small and may be neglected. However the atoms must be close enough such that retardation effects due to the finite speed of the propagation of electromagnetic interactions (discussed in great detail by Power<sup>22</sup>) are not significant. The discussion below briefly describes the computation of the coefficients of the  $1/R^6$ ,  $1/R^8$  and  $1/R^{10}$  terms in the asymptotic expansion of the Van der Waals interaction energy. For more details the reader is referred to the review articles by Dalgarno and Davison<sup>23</sup> and Hirschfelder and Meath<sup>24</sup>.

The perturbation Hamiltonian  $H'$  may be developed in a multipole expansion of the form

$$H' = \sum_{l=0}^{\infty} \sum_{L=0}^{\infty} \frac{V_{lL}}{R^{l+L+1}} \quad (116)$$

where  $V_{lL}$  is given by Dalgarno and Davison<sup>23</sup> and it is associated with the interaction of the  $2^l$ -pole moment of the first atom with the  $2^L$ -pole moment of the second atom. The usual assumption shall be made that the two atoms are neutral and S-states which results in considerable simplification. For a discussion for Van der Waals coefficients for nonspherical atoms see Allison, Burke and Robb<sup>25</sup>. For

neutral atoms  $V_{00} = V_{01} = V_{10} = 0$ . Since the expectation value of any  $2^l$ -pole operator ( $l \geq 1$ ) vanishes for an S-state the first order perturbation energy is identically zero. The second order perturbation energy yields the dominant contribution to the interaction energy and may be expanded in an asymptotic series in the perturbation parameter  $1/R$ .

The second order interaction energy may be expanded in the series

$$E^{(2)} = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - O(R^{-12}) \quad (117)$$

where the  $C_i$ 's arise from multipole-multipole interactions and shall be written in terms of multipole oscillator strengths below. The coefficient  $C_6$  of the leading term in the series is due to the dipole-dipole interaction and may be written as

$$C_6 = \frac{3}{2} \sum_m \sum_n \frac{f_{0m}(\sum_{\mu} P_1(\cos\theta_{\mu})) f_{0n}(\sum_{\nu} r_{\nu} P_1(\cos\theta_{\nu}))}{(\omega_{0m} + \omega_{0n}) \omega_{0m} \omega_{0n}} \quad (118)$$

where  $\mu$  ranges over the electrons of the first atom,  $m$  ranges over all states except  $m = 0$  of the first atom,  $\nu$  ranges over the electrons of the second atom, and  $n$  ranges over all states except  $n = 0$  of the second atom. The above form for writing  $C_6$  is well known but  $C_8$  and  $C_{10}$  are usually expressed in a more awkward form<sup>26</sup>. However, having defined multipole oscillator strengths, the above expression may be easily extended to  $C_8$  and  $C_{10}$ .  $C_8$  is a result of the dipole-quadrupole and quadrupole-dipole interactions. Using Dalgarno and Davison's<sup>23</sup> expression for  $V_{\ell L}$  it can be shown from application of the Wigner-Eckart Theorem that  $C_8$  may be written as

$$C_8 = \frac{15}{4} \sum_m \sum_n \frac{f_{0m}(\sum_{\mu} r_{\mu} P_1(\cos\theta_{\mu})) f_{0n}(\sum_{\nu} r_{\nu}^2 P_2(\cos\theta_{\nu}))}{(\omega_{0m} + \omega_{0n}) \omega_{0m} \omega_{0n}} + \frac{15}{4} \sum_m \sum_n \frac{f_{0m}(\sum_{\mu} r_{\mu}^2 P_2(\cos\theta_{\mu})) f_{0n}(\sum_{\nu} r_{\nu} P_1(\cos\theta_{\nu}))}{(\omega_{0m} + \omega_{0n}) \omega_{0m} \omega_{0n}} \quad (119)$$

$C_{10}$  is the result of the dipole-octupole, the quadrupole-quadrupole and the octupole-dipole interactions. A similar expansion shows that  $C_{10}$  is given by

$$\begin{aligned}
 C_{10} = & 7 \sum_m \sum_n \frac{f_{om}(\sum_{\mu} r_{\mu} P_1(\cos\theta_{\mu})) f_{on}(\sum_{\nu} r_{\nu}^3 P_3(\cos\theta_{\nu}))}{(\omega_{om} + \omega_{on}) \omega_{om} \omega_{on}} \\
 & + \frac{35}{2} \sum_m \sum_n \frac{f_{om}(\sum_{\mu} r_{\mu}^2 P_2(\cos\theta_{\mu})) f_{on}(\sum_{\nu} r_{\nu}^2 P_2(\cos\theta_{\nu}))}{(\omega_{om} + \omega_{on}) \omega_{om} \omega_{on}} \\
 & + 7 \sum_m \sum_n \frac{f_{om}(\sum_{\mu} r_{\mu}^3 P_3(\cos\theta_{\mu})) f_{on}(\sum_{\nu} r_{\nu} P_1(\cos\theta_{\nu}))}{(\omega_{om} + \omega_{on}) \omega_{om} \omega_{on}} .
 \end{aligned} \tag{120}$$

Further coefficients of terms in the second order energy may be obtained in a similar fashion, however third order perturbation theory begins to contribute terms at the  $1/R^{11}$  order of the expansion. Note that the dipole-dipole-dipole term which is order  $1/R^9$  might be expected to be the leading contribution to the third order energy however the parity selection rule forbids this contribution. The product  $\langle 0 | \mu_{\alpha} | n \rangle \langle n | \mu_{\beta} | m \rangle \langle m | \mu_{\gamma} | 0 \rangle$  must clearly vanish since the matrix elements on the ends are allowed only if  $|m\rangle$  and  $|n\rangle$  have odd parity which will cause the middle matrix element to vanish. Similarly the  $1/R^{10}$  contribution vanishes by parity and the leading term in the expansion of the third order energy will be due to the dipole-quadrupole-dipole term which varies as  $1/R^{11}$ .

Static electric interactions shall not be further considered, although there are various other properties which have not been discussed here. These include the interaction of a point charge with an atom as considered by Dalgarno and Stewart<sup>27</sup>. Also of interest is the three-body interaction as discussed by Dalgarno and Davison<sup>23</sup> and Dalgarno<sup>28</sup>. Again, for these interactions, the concept of multipole oscillator strengths is useful for the evaluation of the coefficients of the terms parameterizing the perturbation.

G. APPLICATIONS OF MULTIPOLE OSCILLATOR STRENGTHS TO THE CALCULATION OF EMISSION AND ABSORPTION PROBABILITIES

The interaction of radiation with atoms and molecules may also be treated by a type of multipole expansion, although the approach is somewhat different from that of static electric interactions. For problems involving radiation with a wavelength much longer than the dimensions of the atom or molecule, as is frequently the case, then for electric dipole allowed transitions, the electric dipole term in the multipole expansion provides a good approximation to the interaction. Corrections from additional terms in the multipole expansion may be considered, however these typically prove to be of the same order of significance as the relativistic effects which have been neglected throughout this discussion. Similarly, under long wavelength conditions transitions which are electric dipole forbidden but electric quadrupole or magnetic dipole allowed may be closely approximated by the electric quadrupole or magnetic dipole term in the multipole expansion. Again, multipole corrections to the leading term are of the same order of significance as relativistic effects. If the radiation involved in the interaction has a wavelength comparable to or less than the dimensions of the atom or molecule then the dipole approximation is being violated and it is not clear that the multipole expansion is useful (however, as discussed in Chapter V, the multipole expansion seems to work in this region better than one would expect).

The following discussion shall be limited to only one photon processes (i.e. one photon emission and absorption), although the treatment could be extended to consideration of the multipole expansion of two photon processes (i.e. two photon emission and absorption, and Rayleigh and Raman scattering). Nonrelativistically, the matrix element needed for the computation of one photon transition probabilities is

$$M_{nm}(\vec{k}, \vec{e}) = \langle n | \sum_{i=1}^N e^{i\vec{k} \cdot \vec{r}_i} \vec{e} \cdot \vec{\nabla}_i | m \rangle \quad (121)$$

where  $i$  ranges over the  $N$  electrons of the atom,  $\vec{k}$  is the wave vector of the radiation such that  $|\vec{k}| = k = |\omega_{nm}|$  and  $\vec{e}$  is the unit polarization vector. Note  $\vec{e}$  is perpendicular to  $\vec{k}$  as a consequence of choosing the Lorentz gauge properly<sup>29</sup>. The "oscillator strength" associated with this matrix element may be written

$$f_{nm}(\vec{k}, \vec{e}) = \frac{2}{\omega_{nm}} |M_{nm}(\vec{k}, \vec{e})|^2 \quad (122)$$

and to the accuracy of nonrelativistic quantum mechanics and first order perturbation theory this expression allows the determination of transition probabilities between  $|m\rangle$  and  $|n\rangle$ . Practical considerations usually demand that the wave vector  $\vec{k}$  and polarization vector  $\vec{e}$  be averaged over all possible orientations as described by Bethe and Salpeter<sup>9</sup>, but this procedure is straightforward and shall be ignored here. The computations required can be simplified by expanding the exponential into an infinite series. There are two choices which can be made. The exponential may be expanded in spherical harmonics according to

$$e^{i\vec{k}\cdot\vec{r}_i} = \sum_{l=0}^{\infty} i^l (2l+1) j_l(kr_i) P_l(\cos\theta_i) \quad (123)$$

where  $\theta_i$  is the angle between  $\vec{k}$  and  $\vec{r}_i$ . In contrast to the case of static electric interactions, this spherical harmonic expansion is not particularly useful for obtaining selection rules due to the presence of the factor  $(\vec{e} \cdot \vec{\nabla}_i)$  which multiplies the exponential. The above expansion shall not be considered here, although it has been used by Mizushima<sup>30</sup> to obtain the lowest order approximation to the first non-vanishing electric and magnetic multipole contribution for transitions when lower multipole contributions are forbidden. The second choice for the expansion of the exponential is the simple Taylor series

$$e^{i\vec{k}\cdot\vec{r}_i} = \sum_{l=0}^{\infty} \frac{(i\vec{k}\cdot\vec{r}_i)^l}{l!} \quad (124)$$

which proves to be as useful as the spherical harmonic expansion when

corrections beyond the lowest nonvanishing multipole are desired. To consistently obtain the first correction to  $f_{nm}(\vec{k}, \vec{e})$  beyond the dipole approximation, the matrix element  $M_{nm}$  may be approximated by

$$M'_{nm} = \langle n | \sum_{i=1}^N \left( 1 + i\vec{k} \cdot \vec{r}_i - \frac{(\vec{k} \cdot \vec{r}_i)^2}{2} \right) \vec{e} \cdot \vec{\nabla}_i | m \rangle \quad (125)$$

and the oscillator strength  $f_{nm}(\vec{k}, \vec{e})$  is then approximated by

$$\begin{aligned} f'_{nm}(\vec{k}, \vec{e}) &= \frac{2}{\omega_{nm}} |M'_{nm}(\vec{k}, \vec{e})|^2 \\ &\approx \frac{2}{\omega_{nm}} \left\{ \left| \langle n | \sum_{i=1}^N \vec{e} \cdot \vec{\nabla}_i | m \rangle \right|^2 \right. \\ &\quad + \langle n | \sum_{i=1}^N \vec{e} \cdot \vec{\nabla}_i | m \rangle \langle m | \sum_{j=1}^N \vec{e} \cdot \vec{\nabla}_j \frac{(\vec{k} \cdot \vec{r}_j)^2}{2} | n \rangle \\ &\quad + \langle n | \sum_{i=1}^N \frac{(\vec{k} \cdot \vec{r}_i)^2}{2} \vec{e} \cdot \vec{\nabla}_i | m \rangle \langle m | \sum_{j=1}^N \vec{e} \cdot \vec{\nabla}_j | n \rangle \\ &\quad \left. + \left| \langle n | \sum_{i=1}^N (\vec{k} \cdot \vec{r}_i) (\vec{e} \cdot \vec{\nabla}_i) | m \rangle \right|^2 \right\} \quad (126) \end{aligned}$$

where powers of  $(\vec{k} \cdot \vec{r}_i)$  greater than  $(\vec{k} \cdot \vec{r}_i)^2$  have been neglected and cross terms of the form

$$\langle n | \sum_{i=1}^N \vec{e} \cdot \vec{\nabla}_i | m \rangle \langle m | \sum_{j=1}^N (\vec{e} \cdot \vec{\nabla}_j) (i\vec{k} \cdot \vec{r}_j) | n \rangle \quad (127)$$

vanish by virtue of parity for atoms. For electric dipole allowed transitions the first term in the sum in equation (126) is usually all that is considered. The second two terms form the retardation corrections as considered by Levinger, et.al.<sup>31</sup> The fourth term in the sum may be shown to be composed of electric quadrupole and magnetic dipole contributions as follows. Note that

$$\begin{aligned} (\vec{k} \cdot \vec{r})(\vec{e} \cdot \vec{\nabla}) &= \frac{1}{2} \{ (\vec{k} \cdot \vec{r})(\vec{e} \cdot \vec{\nabla}) + (\vec{k} \cdot \vec{\nabla})(\vec{e} \cdot \vec{r}) \} \\ &\quad + \frac{1}{2} \{ (\vec{k} \cdot \vec{r})(\vec{e} \cdot \vec{\nabla}) - (\vec{k} \cdot \vec{\nabla})(\vec{e} \cdot \vec{r}) \} \\ &= \frac{1}{2} \{ (\vec{k} \cdot \vec{r}) [(\vec{e} \cdot \vec{r}), H] + [(\vec{k} \cdot \vec{r}), H] (\vec{e} \cdot \vec{r}) \} \\ &\quad + \frac{1}{2} \{ (\vec{k} \cdot \vec{r})(\vec{e} \cdot \vec{\nabla}) - (\vec{k} \cdot \vec{\nabla})(\vec{e} \cdot \vec{r}) \} \end{aligned}$$



$$\begin{aligned}
&= \frac{1}{2} \{ (\vec{k} \cdot \vec{r}) (\vec{e} \cdot \vec{r}) H - H (\vec{k} \cdot \vec{r}) (\vec{e} \cdot \vec{r}) \} \\
&\quad + \frac{1}{2} \{ (\vec{k} \cdot \vec{r}) (\vec{e} \cdot \vec{\nabla}) - (\vec{k} \cdot \vec{\nabla}) (\vec{e} \cdot \vec{r}) \}
\end{aligned} \tag{128}$$

where the second step was performed using the relation  $[x_i, H] = \partial/\partial x_i$ . Equation (128) may be further simplified by noting that  $(\vec{k} \cdot \vec{r})$  and  $(\vec{e} \cdot \vec{\nabla})$  commute since  $\vec{k} \cdot \vec{e} = 0$ , hence

$$\begin{aligned}
(\vec{k} \cdot \vec{r}) (\vec{e} \cdot \vec{\nabla}) &= \frac{1}{2} \{ (\vec{k} \cdot \vec{r}) (\vec{e} \cdot \vec{r}) H - H (\vec{k} \cdot \vec{r}) (\vec{e} \cdot \vec{r}) \} \\
&\quad + \frac{i}{2} \{ \vec{k} \times \vec{e} \cdot \vec{l} \}
\end{aligned} \tag{129}$$

where

$$\begin{aligned}
l_1 &= -i \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \\
l_2 &= -i \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \\
l_3 &= -i \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right).
\end{aligned} \tag{130}$$

Therefore the matrix element  $\langle n | \sum_{i=1}^N (\vec{k} \cdot \vec{r}_i) (\vec{e} \cdot \vec{\nabla}_i) | m \rangle$  may be rewritten as

$$\begin{aligned}
&\langle n | \sum_{i=1}^N (\vec{k} \cdot \vec{r}_i) (\vec{e} \cdot \vec{\nabla}_i) | m \rangle \\
&= -\frac{1}{2} \omega_{nm} \langle n | \sum_{i=1}^N (\vec{k} \cdot \vec{r}_i) (\vec{e} \cdot \vec{r}_i) | m \rangle + \frac{i}{2} \langle n | \vec{k} \times \vec{e} \cdot \sum_{i=1}^N \vec{l}_i | m \rangle.
\end{aligned} \tag{131}$$

The first term in equation (131) is the electric quadrupole matrix element. Note that the condition  $\vec{k} \cdot \vec{e} = 0$  implies that the associated operator is "traceless", so it may be written as a sum of spherical quadrupole tensors, i.e.

$$\sum_{i=1}^N (\vec{k} \cdot \vec{r}_i) (\vec{e} \cdot \vec{r}_i) = \sum_{i=1}^N \sum_{\tau=-2}^2 a_{\tau} r_{(i)}^2 Y_{2\tau(i)}. \tag{132}$$

The second term in equation (131) is the magnetic dipole matrix element. The use of nonrelativistic quantum mechanics is already causing errors at this order and the magnetic dipole matrix element is not correct. The problem may be corrected<sup>9</sup> by the replacement

$\vec{l}_i \rightarrow \vec{l}_i + 2\vec{s}_i$  where  $\vec{s}_i$  is the Pauli spin operator vector. Equation (131) can then be substituted back into equation (126) to give the contribution of this matrix element to the oscillator strength. If both the electric quadrupole and magnetic dipole transitions are simultaneously allowed then there will be interference effects (i.e. cross terms) in the oscillator strength<sup>32</sup>, however if one of the states involved in the transition is an S-state then the Wigner-Eckart Theorem can be used to show that the cross terms will vanish. In the Russell-Saunders approximation (L-S coupling) which works fairly well for light atoms, the only magnetic dipole allowed transitions are those between states within the same configuration having the same value of L and S, i.e. within a fine structure level. The only way that magnetic dipole radiation can occur is if the energies of the Zeeman components of a fine structure level are split by a magnetic field. The magnetic field may either be applied externally or it may be supplied internally by a nucleus with a magnetic moment. In the complete relativistic treatment the magnetic oscillator strength between different fine structure levels is nonzero, but is nevertheless very small for light atoms.

The above derivation is valid to only the lowest order in the first nonvanishing multipole, i.e. for electric dipole allowed transitions the electric dipole retardation, electric quadrupole and magnetic dipole contributions are not the only corrections which must be considered. Relativistic effects are again the cause of this discrepancy but this time the wavefunctions instead of the operators are responsible for the problem. The work of Levinger, et.al.<sup>31</sup> indicates that the relativistic effects can be treated perturbatively by using the Pauli approximation which provides relativistic corrections to the nonrelativistic Hamiltonian. The wavefunctions and energies obtained with the modified Hamiltonian are then used to evaluate the "nonretarded" electric dipole contribution to the oscillator strength. For the desired order of accuracy it is sufficient to evaluate the remaining matrix elements using wavefunctions and

energies obtained with the nonrelativistic Hamiltonian.

A rigorous and systematic investigation of higher order corrections to the interaction of radiation with atoms clearly demands that the Dirac equation (or its many electron generalization, the Breit equation, as discussed by Bethe and Salpeter<sup>9</sup>) and the associated relativistic operators, wavefunctions and energies must be used in the derivation. A review of progress on the relativistic calculation of transitions between bound states has been given by Garstang<sup>33</sup>. Relativistic and retardation effects are even more important for the discrete-continuum transitions (i.e. photoionization), which has been examined by Goldman and Drake<sup>34</sup>.

Drake and Goldman<sup>35,36</sup> have recently discussed variational calculations and oscillator strength sum rules for the Dirac equation. The relativistic sum rules obtained (for  $S_R(-1)$ ,  $S_R(0)$ ,  $S_R(1)$ ,  $S_R(2)$ ,  $S_R(3)$ , and  $S_R(4)$ ) are for transitions between a state and all other (both positive and negative energy) states. The contributions of the transitions to the negative energy states are of little interest to atomic physics and these sum rules do not appear to be as useful as nonrelativistic sum rules. Relativistic oscillator strength sums  $S_{R+}(k)$  for transitions from the ground state to only positive energy states would also appear to be less useful because the "inverse energy" asymptotic behavior<sup>9,37-38</sup> of the relativistic oscillator strength density causes  $S_{R+}(k)$  to diverge for  $k \geq 0$  (as opposed to the divergence of the nonrelativistic sum  $S(k)$  for  $k \geq 2.5$ ). Note that Drake and Goldman obtain convergent values of their  $S_R(-1)$ ,  $S_R(0)$ ,  $S_R(1)$ ,  $S_R(2)$ , and  $S_R(3)$  for the hydrogen ground state; this is apparently due to a cancellation of infinities between the positive and negative energy asymptotic oscillator strength contributions to the sums. Apparently the asymptotic form for the oscillator strength density manifests itself at energies much higher than those typically considered in atomic processes; indeed Drake and Goldman's variational calculations were unable to detect any hint of the divergence of  $S_{R+}(0)$  using their variational basis. One possible

approach to obtaining useful relativistic corrections to sum rules might be to use Levinger, et.al.'s<sup>31</sup> method of replacing the nonrelativistic Hamiltonian in the sum rule derivations with the Pauli approximation corrected Hamiltonian and then to proceed as usual.

The effects of the quantization of the radiation field can be important in atoms and molecules as exhibited by the Lamb shift, however this problem is beyond the scope of the present discussion. Although field quantization should be performed consistent with relativity, there is no covariant theory for the many-particle interactions present in atoms and molecules. Non-covariant quantum mechanics as discussed by Power<sup>39</sup> must be used and a review article by Woolley<sup>40</sup> has examined recent progress on the subject (including the multipole expansion of the interaction Hamiltonian).

#### H. QUADRUPOLE OSCILLATOR STRENGTH SUM RULES

In the previous two sections it has been shown that the quadrupole oscillator strengths are of some interest in connection with static electric field problems and radiation problems. In this section the "velocity" and "acceleration" forms of the "length" quadrupole operator  $r^2Y_{20}$  shall be presented for atoms. In general the other four quadrupole operators  $r^2Y_{22}$ ,  $r^2Y_{21}$ ,  $r^2Y_{2-1}$  and  $r^2Y_{2-2}$  can also appear in matrix elements however the Wigner-Eckart Theorem relates these to matrix elements of the operator  $r^2Y_{20}$ . The sum rules associated with  $r^2Y_{20}$  for a given state shall then be discussed. If the state is not an S-state then unfortunately the sum rules can pick up contributions from intermediate states with more than one possible value of the angular momentum quantum number L. This apparently prevents usage of the Wigner-Eckart Theorem and the oscillator strength sums for  $r^2Y_{20}$  to obtain oscillator strength sums as the other four quadrupole operators except when the state under consideration is an S-state. Finally, some values of quadrupole oscillator strength sums for the ground state of atomic hydrogen are presented.

The quadrupole operator  $r^2 Y_{20}$  for the present purposes may be most conveniently expressed as the "harmonic polynomial"<sup>41-42</sup> in cartesian coordinates given by

$$r^2 Y_{20} = \frac{1}{4} \sqrt{\frac{5}{\pi}} (2z^2 - x^2 - y^2). \quad (133)$$

The operator of interest for many-electron atoms shall be denoted by A and is the above operator summed over all electrons, i.e.

$$A = \sum_{i=1}^N \frac{1}{4} \sqrt{\frac{5}{\pi}} (2z_i^2 - x_i^2 - y_i^2). \quad (134)$$

The N-electron Hamiltonian shall be taken to be

$$H = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_{i < j} \frac{1}{r_{ij}}. \quad (135)$$

The "velocity form of A shall be denoted by B where

$$\begin{aligned} B &= [A, H] \\ &= \frac{1}{4} \sqrt{\frac{5}{\pi}} \sum_i (4z_i \frac{\partial}{\partial z_i} - 2x_i \frac{\partial}{\partial x_i} - 2y_i \frac{\partial}{\partial y_i}). \end{aligned} \quad (136)$$

Similarly the "acceleration" form of A shall be denoted by C where

$$\begin{aligned} C &= \frac{1}{4} \sqrt{\frac{5}{\pi}} \sum_i \left\{ \frac{2Z}{r_i^3} (2z_i^2 - x_i^2 - y_i^2) + 2 \left( 2 \frac{\partial^2}{\partial z_i^2} - \frac{\partial^2}{\partial x_i^2} - \frac{\partial^2}{\partial y_i^2} \right) \right\} \\ &\quad - \frac{1}{4} \sqrt{\frac{5}{\pi}} \sum_{i < j} \frac{1}{r_{ij}^3} [4(z_i - z_j)^2 - 2(x_i - x_j)^2 - 2(y_i - y_j)^2]. \end{aligned} \quad (137)$$

Note that A and C are Hermitian while B is anti-Hermitian. A, B, and C may be used to construct oscillator strength sum rules as discussed by Jackiw<sup>43</sup> and one obtains

$$S(-1; A) = \langle 0 | A A | 0 \rangle \quad (138)$$

$$S(0; A) = -\langle 0 | A B | 0 \rangle \quad (139a)$$

$$= -\frac{1}{2} \langle 0 | [A, B] | 0 \rangle \quad (139b)$$

$$S(1;A) = -\langle 0|BB|0\rangle \quad (140)$$

$$S(2;A) = \langle 0|BC|0\rangle \quad (141a)$$

$$= \frac{1}{2}\langle 0|[B,C]|0\rangle \quad (141b)$$

$$S(3;A) = \langle 0|CC|0\rangle \quad (142)$$

where the commutator forms of  $S(0;A)$  and  $S(2;A)$  have been obtained by noting that the matrix elements are self conjugate since the oscillator strength sums to which they are equal must be real. The practical advantage in using the commutator forms of the matrix elements is that the integrals which must be computed are simpler. If  $S(0;A)$  is evaluated using equation (139a) then the worst integrals encountered are two-electron integrals while if equation (139b) is used only one-electron integrals appear. Similarly in evaluating  $S(2;A)$  the worst integrals encountered in equations (141a) and (141b) are three-electron and two-electron integrals respectively.

The sum rules listed for the quadrupole operator may readily be applied to obtain the quadrupole oscillator strength sums for the ground state of atomic hydrogen. The operator  $r^2 P_2(\cos\theta)$  is simply related to  $r^2 Y_{20}$  by

$$r^2 P_2(\cos\theta) = \sqrt{\frac{4\pi}{5}} r^2 Y_{20} \quad (143)$$

and the sum rules for this more common choice of the quadrupole operator differ from those already derived by the obvious constant factor ( $4\pi/5$ ). Application of the sum rules yield

$$S(3; r^2 P_2(\cos\theta)) = \frac{104}{5}$$

$$S(2; r^2 P_2(\cos\theta)) = \frac{28}{5}$$

$$S(1; r^2 P_2(\cos\theta)) = \frac{24}{5}$$

$$S(0; r^2 P_2(\cos \theta)) = 6$$

$$S(-1; r^2 P_2(\cos \theta)) = 9.$$

These results can also be obtained by the technique of Lamm and Szabo<sup>17</sup> and all sums except  $S(3; r^2 P_2(\cos \theta))$  can also be obtained using a variational basis as described earlier in Section D. In addition, the following five sums have been calculated using Bell's<sup>16</sup> technique.

$$S(-2; r^2 P_2(\cos \theta)) = 15$$

$$S(-3; r^2 P_2(\cos \theta)) = \frac{107}{4}$$

$$S(-4; r^2 P_2(\cos \theta)) = \frac{2,399}{48}$$

$$S(-5; r^2 P_2(\cos \theta)) = \frac{55,631}{576}$$

$$S(-6; r^2 P_2(\cos \theta)) = \frac{6,615,571}{34,560}.$$

These sums may also be obtained by the variational method or the technique of Lamm and Szabo.

#### I. THE VARIATIONAL CALCULATION OF LOGARITHMIC MEAN EXCITATION ENERGIES

The logarithmic mean excitation energies,  $L(k)$ , defined by

$$L(k) = \sum_n f_{on} \omega_{on}^k \ln \omega_{on} \quad (144)$$

are of physical interest for  $k = -1, 0, 1$  and  $2$ . As before, with the dipole oscillator strength sums  $S(k)$ , a variational approach to evaluating the  $L(k)$  is desirable because all states are not usually known.

It is convenient to introduce the expression

$$J(k) = \frac{3}{2} \sum_n \frac{f_{0n} \omega_{0n}}{\omega_{0n} + k} \quad (145)$$

to simplify the derivation.  $J(k)$  is useful because it is straightforward to show the  $L(2)$ ,  $L(1)$ ,  $L(0)$  and  $L(-1)$  can be written in terms of  $J(k)$  as

$$L(2) = \frac{2}{3} \lim_{k_0 \rightarrow \infty} \left[ \left( \int_0^{k_0} J(k) k dk \right) - S(1)k_0 + S(2) \ln k_0 \right] \quad (146)$$

$$L(1) = \frac{2}{3} \lim_{k_0 \rightarrow \infty} \left[ - \left( \int_0^{k_0} J(k) dk \right) + S(1) \ln k_0 \right] \quad (147)$$

$$L(0) = \frac{2}{3} \lim_{k_0 \rightarrow 0} \left[ \left( \int_{k_0}^{\infty} \frac{J(k)}{k} dk \right) + S(0) \ln k_0 \right] \quad (148)$$

$$L(-1) = \frac{2}{3} \lim_{k_0 \rightarrow 0} \left[ - \left( \int_{k_0}^{\infty} \frac{J(k)}{k^2} dk \right) + \frac{S(0)}{k_0} + S(-1) \ln k_0 \right]. \quad (149)$$

If it is possible to provide a technique to approximately solve for  $J(k)$  then equations (146) - (149) may be used to evaluate the logarithmic sums; indeed Chan and Dalgarno<sup>44</sup> used this technique to calculate  $L(1)$  for the ground state of atomic helium. Note that  $S(-1)$ ,  $S(0)$ ,  $S(1)$  and  $S(2)$  are known in terms of ground state expectation values so they do not present any problem in the evaluation of equations (146) - (149).

As written in equation (145),  $J(k)$  requires a knowledge of all states for its evaluation. However  $J(k)$  may be expressed as

$$J(k) = - \langle \Theta | \vec{\nabla} | \Psi_0 \rangle \quad (150)$$

$$\vec{\nabla} \equiv \sum_{i=1}^N \vec{\nabla}_i$$

where  $\Theta = \Theta(r, k)$  is the solution to the inhomogeneous differential equation

$$(H - E_0 + k) | \Theta \rangle + \vec{\nabla} | \Psi_0 \rangle = 0. \quad (151)$$

Clearly  $| \Theta \rangle$  may be formally solved in terms of the complete set of eigenfunctions of  $H$  by



$$|\Theta\rangle = - \sum_n \frac{\langle \Psi_n | \nabla | \Psi_0 \rangle}{E_n - E_0 + k} |\Psi_n\rangle. \quad (152)$$

Hence,

$$\begin{aligned} J(k) &= \sum_n \frac{|\langle \Psi_n | \nabla | \Psi_0 \rangle|^2}{E_n - E_0 + k} \\ &= \frac{3}{2} \sum_n \frac{f_{0n} \omega_{0n}}{\omega_{0n} + k} \end{aligned}$$

which verifies the claim.

Since all the states are not usually known, an alternative method is needed to obtain  $J(k)$ .  $|\Theta\rangle$  may be obtained variationally, after observing that solving equation (151) is equivalent to finding the  $|\xi\rangle$  for which the functional

$$w(\xi, k) = \langle \xi | E_0 - H - k | \xi \rangle - 2 \langle \xi | \nabla | \Psi_0 \rangle \quad (153)$$

is stationary, i.e. the functional is stationary for  $\xi = \Theta$ . Proofs of all these statements are analogous to those given in Section B.

Following the development given in Section B leads to the first variation  $\delta w$  and the second variation  $\delta^2 w$  of the functional  $w$  about  $\Theta$  as

$$\delta w = 2\epsilon \langle \Phi | ((E_0 - H - k) | \Theta \rangle - \nabla | \Psi_0 \rangle) \quad (154)$$

and

$$\delta^2 w = \epsilon^2 \langle \Phi | E_0 - H - k | \Phi \rangle \quad (155)$$

and all higher variations vanish. Note that the exact value of  $w(k)$  (i.e. when  $\xi = \Theta$ ) is  $J(k)$ .

In practice  $|\Theta\rangle$  may be approximated by a trial function  $|\Theta'\rangle$  which has linear variational parameters (which are functions of  $k$ ), i.e.

$$|\Theta'\rangle(\vec{r}, k) = \sum_{i=1}^M a_i(k) \phi_i(\vec{r}) \quad (156)$$

Finding the  $|\Theta'\rangle$  for which  $w(\Theta', k)$  is stationary is accomplished by solving the set of simultaneous linear equations

$$\frac{\partial w(\Theta', k)}{\partial a_i} = 0 \quad i = 1, 2, \dots, M \quad (157)$$

The  $k$  dependence can be handled in either of two ways:

1. Compute  $a_i(k)$  for specific numerical values of  $k$ .
2. The  $k$  dependence can be treated analytically by converting the system of equations (157) into a set of eigenvalue problems. This can be done for an arbitrary basis<sup>45</sup> but here Kolker and Michels<sup>46</sup> technique shall be followed which requires that the trial function basis satisfies

$$\langle \phi_i | \phi_j \rangle = \delta_{ij}$$

and

$$\langle \phi_i | H | \phi_j \rangle = \delta_{ij} \epsilon_i.$$

Then

$$0 = \frac{\partial w(\Theta', k)}{\partial a_i} = 2 \langle \phi_i | E_0 - H - k | \phi_i \rangle a_i - 2 \langle \phi_i | \nabla | \psi_0 \rangle \quad (158)$$

for  $i = 1, 2, \dots, M$ , which implies

$$0 = (E_0 - \epsilon_i - k) a_i - \langle \phi_i | \nabla | \psi_0 \rangle \quad i = 1, 2, \dots, M \quad (159)$$

and the  $a_i$ 's are determined by

$$a_i = \frac{-\langle \phi_i | \nabla | \psi_0 \rangle}{\epsilon_i - E_0 + k} \quad (160)$$

Therefore the  $|\Theta'\rangle$  for which  $w(\Theta', k)$  is stationary is given by

$$|\Theta'\rangle = - \sum_i \frac{\langle \phi_i | \nabla | \psi_0 \rangle}{\epsilon_i - E_0 + k} |\phi_i\rangle \quad (161)$$

and the associated value of  $w$  ( $=w(k)$ ) is

$$\begin{aligned}
w(k) &= \langle \Theta' | E_0 - H - k | \Theta' \rangle - 2 \langle \Theta' | \nabla | \Psi_0 \rangle \\
&= \sum_i \frac{K \phi_i | \nabla | \Psi_0 \rangle|^2}{\epsilon_i - E_0 + k} \\
&= \frac{3}{2} \sum_i \frac{f'_{oi} \omega'_{oi}}{\omega'_{oi} + k}
\end{aligned} \tag{162}$$

where  $\omega'_{oi} = \epsilon_i - E_0$  and

$$f'_{oi} = \frac{2}{3} \frac{K \phi_i | \nabla | \Psi_0 \rangle|^2}{\omega'_{oi}} .$$

Using the same kind of arguments presented in Section B, it follows from equation (155) that  $w(k) \leq J(k)$  for  $k \geq 0$ . Clearly when  $k \geq 0$  the second variation  $\delta^2 w$  of  $w$  is negative for arbitrary (non-zero)  $\epsilon | \Phi \rangle$ , hence any deviation from the exact stationary position (where  $w(k) = J(k)$ ) to the trial function stationary position will tend to decrease  $w(k)$ .  $J(k)$  is a global maximum to  $w(k)$  (i.e.  $J(k)$  is an upper bound to  $w(k)$  constructed from any trial function basis) because all variations beyond the second vanish. Therefore the claim that  $w(k) \leq J(k)$  for  $k \geq 0$  follows.

Upon obtaining  $w(k)$ ,  $S(2)$ ,  $S(1)$ ,  $S(0)$  and  $S(-1)$ , all information needed to calculate the logarithmic sums from equations (146) - (149) is at hand. Assuming that the  $S(2)$ ,  $S(1)$ ,  $S(0)$  and  $S(-1)$  values are exact implies that replacing  $J(k)$  in these expressions by  $w(k)$  (which bounds  $J(k)$  from below) will lead to bounds on the  $L(k)$ . It is easily seen that the variational calculation must

- 1) bound  $L(2)$  from below,
- 2) bound  $L(1)$  from above,
- 3) bound  $L(0)$  from below, and
- 4) bound  $L(-1)$  from above.

The unpleasant task of taking limits in order to obtain the  $L(k)$  can be avoided entirely if the trial function basis is chosen properly. First one must define the effective logarithmic sum  $L'(k)$

by

$$L'(k) = \sum_i f'_{oi} \omega'_{oi}{}^k \ln \omega'_{oi} \quad (163)$$

and the effective oscillator strength sum  $S'(k)$  by

$$S'(k) = \sum_i f'_{oi} \omega'_{oi}{}^k. \quad (164)$$

Then it is easily seen that

$$L'(2) = \frac{2}{3} \lim_{k_0 \rightarrow \infty} \left[ \left( \int_0^{k_0} w(k) k dk \right) - S'(1) k_0 + S'(2) \ln k_0 \right] \quad (165)$$

$$L'(1) = \frac{2}{3} \lim_{k_0 \rightarrow \infty} \left[ - \left( \int_0^{k_0} w(k) dk \right) + S'(1) \ln k_0 \right] \quad (166)$$

$$L'(0) = \frac{2}{3} \lim_{k_0 \rightarrow 0} \left[ \left( \int_{k_0}^{\infty} \frac{w(k)}{k} dk \right) + S'(0) \ln k_0 \right] \quad (167)$$

$$L'(-1) = \frac{2}{3} \lim_{k_0 \rightarrow 0} \left[ - \left( \int_{k_0}^{\infty} \frac{w(k)}{k^2} dk \right) + \frac{S'(0)}{k_0} + S'(-1) \ln k_0 \right]. \quad (168)$$

From equations (165) - (168) it follows that if the basis  $\{\phi_i\}$  can be chosen such that  $S'(k) = S(k)$  for  $k = -1, 0, 1, 2$  then evaluating equations (146) - (149) with  $J(k)$  replaced by  $w(k)$  is equivalent to the expression (163). For simplicity equation (163) is preferred over equations (165) - (168) for purposes of evaluation. Fortunately Dalgarno and Epstein have determined<sup>8</sup> that if the functions  $\bar{r}|\psi_0\rangle$  and  $\bar{v}|\psi_0\rangle$  are contained in the trial function space then the requirement that  $S'(k) = S(k)$  for  $k = -1, 0, 1, 2$  is satisfied.

Collecting results, it has been determined that if a basis is constructed which spans  $\bar{r}|\psi_0\rangle$  and  $\bar{v}|\psi_0\rangle$  and satisfies the conditions

$$\langle \phi_i | \phi_j \rangle = \delta_{ij}$$

and

$$\langle \phi_i | H | \phi_j \rangle = \delta_{ij} \epsilon_i$$

then the approximations  $L'(k)$  to the logarithmic sums  $L(k)$  may be

written as

$$L'(k) = \frac{2}{3} \sum_{i=1}^M |\langle \phi_i | \vec{\nabla} | \psi_0 \rangle|^2 (\epsilon_i - E_0)^{k-1} \ln(\epsilon_i - E_0). \quad (169)$$

As described earlier,  $L'(2)$  bounds  $L(2)$  from below,  $L'(1)$  bounds  $L(1)$  from above,  $L'(0)$  bounds  $L(0)$  from below and  $L'(-1)$  bounds  $L(-1)$  from above.

In the previous discussion the variational principle for the functional  $J(k)$  led to expressions involving the velocity form of the dipole matrix element. It should be noted that another useful functional,  $J'(k)$ , may be expressed in terms of the length form of the dipole matrix element where

$$J'(k) = \frac{3}{2} \sum_n \frac{f_{on}}{\omega_{on}(\omega_{on} + k)}. \quad (170)$$

Then

$$J'(k) = -\langle \Delta | \vec{r} | \psi_0 \rangle \quad (171)$$

$$\vec{r} = \sum_{i=1}^N \vec{r}_i$$

where  $\Delta(\vec{r}, k)$  is the solution to

$$(H - E_0 + k) | \Delta \rangle + \vec{r} | \psi_0 \rangle = 0. \quad (172)$$

This is the form in which the variational principle for the dynamic polarizability is usually posed. A similar treatment to that previously performed yields approximations  $L''(k)$  to the logarithmic sums of the form

$$L''(k) = \frac{2}{3} \sum_{i=1}^M |\langle \phi_i | \vec{r} | \psi_0 \rangle|^2 (\epsilon_i - E_0)^{k+1} \ln(\epsilon_i - E_0) \quad (173)$$

with the same bounding behavior on  $L(k)$  as that which  $L'(k)$  had. But the results of Dalgarno and Epstein<sup>8</sup> show that if  $\vec{r} | \psi_0 \rangle$  is spanned by the basis then

$$\langle \phi_i | \vec{\nabla} | \psi_0 \rangle = \langle \phi_i | \vec{r} | \psi_0 \rangle (\epsilon_i - E_0). \quad (174)$$

Furthermore if  $\vec{r}|\psi_0\rangle$  and  $\vec{v}|\psi_0\rangle$  are both contained in the space of trial functions then

$$\sum \langle \phi_i | \frac{\vec{r}}{r^3} | \psi_0 \rangle = \sum \langle \phi_i | \vec{v} | \psi_0 \rangle (\epsilon_i - E_0) \quad (175)$$

$$= \langle \phi_i | \vec{r} | \psi_0 \rangle (\epsilon_i - E_0)^2. \quad (176)$$

Since the basis has been chosen to span both  $\vec{r}|\psi_0\rangle$  and  $\vec{v}|\psi_0\rangle$  it immediately follows that  $L''(k) = L'(k)$ . Therefore both variational calculations lead to identical results.

In fact if the effective oscillator strength is computed in any of the possible forms the same result will be obtained, i.e. length-length, length-velocity, length-acceleration, velocity-velocity, velocity-acceleration, and acceleration-acceleration will all yield the same result for a properly chosen basis. Unfortunately, the identity between the length, velocity and acceleration formulations of the dipole matrix element requires that the ground state be exact, which is of course impossible to achieve except in the case of atomic hydrogen. Little can be said about the case where the ground state is not exact but this question has been examined by Redmon and Browne<sup>47</sup> and Klein and DeVries<sup>48</sup>.

#### J. VARIATIONAL CALCULATIONS OF LOGARITHMIC MEAN EXCITATION ENERGIES AND $C_6$ FOR ATOMIC HYDROGEN

Using the variational technique described in Section I, calculations have been performed on the logarithmic mean excitation energies for the ground state of atomic hydrogen. Effective states generated in the course of the calculations were also used to determine  $C_6$ , the coefficient of the  $1/R^6$  term in the Van der Waals interaction energy.

The trial function basis sets were chosen such that they are characterized by the integers  $j$  and  $n$ , and consist of basis functions labeled by  $i$  and  $j$  according to

$$\phi_i^{(j)} = r^{\frac{i}{j}} \cos\theta \Psi_0 \quad i = 0, 1, \dots, n-1 \quad (177)$$

where  $\Psi_0$  is the ground state of atomic hydrogen. Calculations were performed for  $j = 1, 2,$  and  $4$  (i.e. integer, half-integer, and quarter integer powers of the variable  $r$ ) with  $n$  ranging up to  $30$  for  $j = 1,$  up to  $27$  for  $j = 2,$  and up to  $18$  for  $j = 4.$  Note that  $n$  is equal to the dimensionality of the basis set. The upper limit on  $n$  in each case was chosen to avoid the numerical ill-conditioning problems which could be detected for higher values of  $n.$  The generation of an orthonormal basis in which the representation of the Hamiltonian is diagonal, as required by the variational principle, was performed numerically using a secular equation solver. The calculations were performed to double precision (28 digits). All integrals may be evaluated analytically in terms of gamma functions and the necessary high precision values for the rational fraction arguments encountered have been tabulated by Abramowitz and Stegun<sup>49</sup> and Galant and Byrd<sup>50</sup>.

The results for the logarithmic sums are presented in Table 8 for the largest  $j = 1, 2,$  and  $4$  bases used. Results are presented in Rydbergs rather than atomic units to facilitate easy comparison with Shimamura's<sup>51,52</sup> results. Note that the bounding behavior is consistent with that proved in the previous section. The variational solutions bound  $L(2)$  from below,  $L(1)$  from above,  $L(0)$  from below and  $L(-1)$  from above. The quarter-integer power basis yields the best value of  $L(2)$  while the half-integer power basis yields the best values of  $L(1), L(0)$  and  $L(-1).$  In spite of the fact that the integer power basis contains the most terms it nevertheless yields the poorest results in all cases. Apparently what is happening is that in order to represent  $J(k)$  for higher values of the parameter  $k$  it becomes more important for the basis to adequately span the space of functions in the region close to the nucleus. In this region the integer power basis looks more linearly dependent than does the half-integer or quarter-integer power bases. This would seem to explain why  $L(2)$  (which is most sensitive to the high  $k$  behavior of  $J(k)$ ) is

Table 8

Basis (j,n)	L(2)
(1,30)	15.435
(2,27)	15.890
(4,18)	15.911
Actual Value <sup>51</sup>	15.915
Basis (j,n)	L(1)
(1,30)	.76124947
(2,27)	.76116420
(4,18)	.76116421
Actual Value <sup>51</sup>	.76116413
Basis (j,n)	L(0)
(1,30)	.09698173225
(2,27)	.09698180914
(4,18)	.09698180898
Actual Value <sup>51</sup>	.09698180915
Basis (j,n)	L(-1)
(1,30)	-.07325375520645
(2,27)	-.07325375537291
(4,18)	-.07325375537059
Actual Value <sup>51</sup>	-.07325375537292



most accurately calculated using the quarter-integer power basis.

Logarithmic sums can also be calculated using various approaches different from that previously described. The most accurate calculations performed on atomic hydrogen are due to Shimamura<sup>51</sup>, who has calculated  $L(2)$  to 15 digits,  $L(1)$  to 14 digits, and  $L(0)$  and  $L(-1)$  to 13 digits using Coulomb Green's functions. Lieber<sup>53</sup> and Huff<sup>54</sup> have calculated  $L(2)$  for atomic hydrogen using Lie algebraic techniques. In contrast to the previously described variational method, these approaches cannot be extended to more complicated atoms or molecules. Other methods which do generalize include the techniques to obtain  $L(k)$  from known  $S(k)$ : 1) bounds presented here in Chapter II, 2) Pekeris'<sup>55</sup> and Garcia's<sup>56</sup> interpolation schemes for obtaining  $L(2)$ , and 3) a spline method to obtain  $L(0)$  and  $L(1)$  proposed by Peek<sup>57</sup>. Also, Chan and Dalgarno<sup>44</sup> calculated  $L(0)$  and  $L(1)$  for helium using a variational technique similar to that presented here. Finally, Schwartz's calculation of  $L(2)$  for helium<sup>58</sup> involved calculating  $J(k)$  separately within three regions of the range of  $k$ , then numerically integrating over  $k$  the values obtained to achieve the final result. For the low  $k$  region Schwartz's variational calculation of  $J(k)$  is related to the method described in this work. For the intermediate  $k$  region he built explicit  $k$  dependence into the basis functions and for the high  $k$  region he used an asymptotic solution to  $J(k)$  which will be described in detail in Chapter IV.

The integer power basis (i.e.  $j = 1$ ) of dimension  $n$  has the special property that the resulting effective oscillator strength distribution is exactly the same as that obtained from  $S(2)$ ,  $S(1)$ , ...,  $S(-2n+3)$  using the technique described in Chapter II. This clearly follows from the proof presented which shows that such a basis satisfies precisely these sums. Effective distributions constructed from such a set of sums were shown to allow the determination of a lower bound on  $C_6$ . For the present case of atomic hydrogen, the integer power method provides an extremely convergent and numerically stable method for generating the effective oscillator strength dis-

tributions to be used for evaluating  $C_6$ . The values listed in Table 9 were obtained by substituting the effective oscillator strengths  $f'_{0i}$  and energy differences  $\omega'_{0i}$  obtained from the variational basis into the expression

$$C_6 = \frac{3}{2} \sum_{i=1}^n \sum_{j=1}^n \frac{f'_{0i} f'_{0j}}{(\omega'_{0i} + \omega'_{0j}) \omega'_{0i} \omega'_{0j}} . \quad (178)$$

Values are expressed in atomic units. Convergence has been reached to 18 digits and the value obtained is  $C_6 = 6.49902670540583931$ . Various checks have been performed to insure that roundoff has not introduced errors to the number of digits claimed, including a check that the effective distributions satisfied certain of the oscillator strength sums to more than 18 digits. The value for  $C_6$  listed above agrees with the first 18 digits of a 28 digit value given by Margoliash and Meath<sup>59</sup>, however they do not state the number of significant digits in their answer.

Table 9

Basis (j,n)	
(1,5)	6.499007944003187367
(1,10)	6.499026705137112160
(1,15)	6.499026705405408842
(1,20)	6.499026705405834730
(1,25)	6.499026705405839178
(1,26)	6.499026705405839240
(1,27)	6.499026705405839273
(1,28)	6.499026705405839290
(1,29)	6.499026705405839300
(1,30)	6.499026705405839305

K. CALCULATIONS OF PHOTOIONIZATION CROSS SECTIONS USING SQUARE INTEGRABLE BASIS FUNCTIONS

The total photoionization cross section for the absorption of a photon and subsequent excitation of one or more electrons into the continuum is, in the dipole approximation, directly proportional to the dipole oscillator strength density in the continuum. The total cross section,  $\sigma$ , is related to the oscillator strength density  $df/d\epsilon$  through the equation

$$\sigma = \frac{\pi e^2 h}{m c} \frac{df}{d\epsilon} \quad (179)$$

as shown by Fano and Cooper<sup>10</sup>. To evaluate the oscillator strength density using a direct approach would require computing dipole matrix elements between the initial bound state and continuum wavefunctions. The bound state can be computed using the variational principle on the energy which of course cannot be used for the continuum state. However the continuum wavefunctions can be calculated using the Hulthen-Kohn variational principle<sup>60-61</sup> on the phase shift (e.g. the  $H^-$  calculation by Geltman<sup>62</sup>) or the close coupling method<sup>63</sup>.

The need to calculate continuum wavefunctions can be avoided entirely by an indirect approach to computing oscillator strength densities using effective discrete states. The previously described effective oscillator strength distributions, constructed either from a set of  $S(k)$  or using a square integrable (as opposed to non-square integrable continuum wavefunctions) variational basis, include effective discrete states above the ionization threshold, i.e. in a region where the oscillator strength is actually a continuous density. Langhoff has proposed<sup>3-5</sup> that obtaining a density by applying Stieltjes and Tchebycheff smoothing procedures to effective discrete states constructed from a set of  $S(k)$  should furnish a good approximation to the actual density. Here an alternative smoothing procedure is applied to the discrete states obtained from the integer,

half-integer, and quarter-integer power bases used in the previous section. The approximate oscillator strength densities so obtained are then compared with the exact result calculated in Section E.

Langhoff's Stieltjes and Tchebycheff procedures are implemented as follows. Given a set of  $n$  oscillator strengths  $f_i$  and  $n$  associated energies  $\epsilon_i$ , the Stieltjes smoothing procedure defines the density  $df/d\epsilon$  as

$$\frac{df}{d\epsilon} = \frac{1}{2} \frac{(f_{i+1} + f_i)}{\epsilon_{i+1} - \epsilon_i} \quad \epsilon_i < \epsilon < \epsilon_{i+1} \quad (180)$$

and

$$\frac{df}{d\epsilon}(\epsilon) = 0 \quad \text{for } \epsilon < \epsilon_1 \text{ and } \epsilon > \epsilon_n. \quad (181)$$

This method results in a discontinuous histogram function for the density. The Tchebycheff procedure first requires determining the function  $f_0(\epsilon)$  which is constructed by solving for the  $f_0(\epsilon)$ ,  $f_1(\epsilon)$ ,  $f_2(\epsilon)$ , ...,  $f_n(\epsilon)$  and associated  $\epsilon_0(=\epsilon)$ ,  $\epsilon_1(\epsilon)$ ,  $\epsilon_2(\epsilon)$ , ...,  $\epsilon_n(\epsilon)$  which satisfies a set of  $2n+1$   $S(k)$ . This may be done by choosing a value for  $\epsilon$ , solving for the resulting set of equations, and repeating the process for a sequence of closely spaced values of  $\epsilon$  over the desired range. Then the approximate oscillator strength density is defined according to

$$\frac{df}{d\epsilon}(\epsilon) = \frac{1}{2} \frac{df_0(\epsilon)}{d\epsilon} + \sum_{i \text{ } (\epsilon_i < \epsilon)} \frac{df_i(\epsilon)}{d\epsilon} \quad (182)$$

where the derivatives with respect to  $f_0(\epsilon)$ ,  $f_1(\epsilon)$ , ... must be obtained numerically. This procedure can result in an extremely smooth distribution if the grid size (i.e. the separation between the values of  $\epsilon$  for which  $f_i(\epsilon)$  has been computed) is taken to be sufficiently small. Since the grid size is a matter of choice, limited only by how many calculations one is willing to perform, this does not present a problem. Note that smooth densities do not necessarily imply accurate results and in fact Tchebycheff distributions obtained from

a large number of moments have been found to yield unreliable results<sup>64</sup>.

Here an alternative smoothing method is proposed. The procedure converts an effective discrete distribution into a continuous density, hence it is smoother than the Stieltjes histogram method. The approximate density is given in terms of the discrete oscillator strengths  $f_i$  and associated energies  $\epsilon_i$  by

$$\frac{df}{d\epsilon}(\epsilon) = \frac{2f_i(\epsilon_{i+1} - \epsilon)}{(\epsilon_{i+1} - \epsilon_{i-1})(\epsilon_{i+1} - \epsilon_i)} + \frac{2f_{i+1}(\epsilon - \epsilon_i)}{(\epsilon_{i+2} - \epsilon_i)(\epsilon_{i+1} - \epsilon_i)} \quad \epsilon_i < \epsilon < \epsilon_{i+1} \quad (183)$$

The function is essentially the result of smoothing each oscillator strength "spike" into a triangular shaped density with a base extending from the energies of the adjacent lower to adjacent higher oscillator strengths, then simply summing contributions of overlapping triangles. The altitude of the individual triangles is determined by requiring the integrated oscillator strength of a triangle to equal that of the associated "spike".

Tables 10, 11, and 12 contain values of the oscillator strength density calculated from discrete distributions obtained from the integer, half-integer, and quarter-integer power bases respectively. Densities have been listed only at those energies where the original discrete oscillator strengths were located. The vertices at which the linear segments (of the function defined in equation (183)) are connected are located at these energies, so to obtain the value between two adjacent listed values linear interpolation is all that is needed. As can be seen from the listed energies, the spectra associated with the three bases are significantly different. The energies of the integer power basis spectrum are relatively closely spaced and the energy of the highest state is 759 a.u. The energies of the half-integer power basis are more widely separated and the energy of the highest state is  $2.95 \times 10^5$  a.u. The energies of the quarter-integer power basis are spaced the farthest apart and the

energy of the highest state is  $7.36 \times 10^7$  a.u. The highest states do not appear in the tables since the smoothing procedure requires states both below and above a state to obtain the approximate density. Note also that the discrete states generated by the variational procedure which lie below the ionization threshold have not been listed since in this region the states should, in fact, be discrete. The three spectra seem consistent with the calculations of the  $L(k)$  which indicate that the distribution associated with the half-integer power basis provides a set of states which represents the "medium energy region" more adequately than the other two bases. Also, the quarter-integer power basis furnishes the representation of the "high energy region".

The smoothing technique described here tends to work well near threshold but begins to fail at higher energies where the pseudostates become spaced farther apart. Apparently this is due to the fact that a piecewise linear approximation is inadequate to represent a nonlinear function over a long range. An alternative approach to obtaining the high energy behavior of the dipole oscillator density using a combination of asymptotic and moment methods will be described in Chapter V.

Table 10

30 Term, Integer Power Basis

Pseudostate Energy $\epsilon$ (a.u.)	$\frac{df}{d\epsilon}$ (Exact)	$\frac{df}{d\epsilon}$ (From Pseudostates after smoothing)	% Error
.0019	1.547	1.545	-.1%
.0185	1.418	1.414	-.3%
.0395	1.275	1.270	-.4%
.0653	1.124	1.119	-.5%
.0966	.972	.967	-.5%
.1343	.823	.818	-.6%
.1797	.681	.676	-.6%
.2344	.550	.546	-.7%
.3007	.432	.429	-.8%
.3815	.330	.327	-.9%
.4807	.244	.242	-1.0%
.6042	.174	.172	-1.1%
.7597	.119	.117	-1.3%
.9589	.0776	.0763	-1.5%
1.219	.0478	.0469	-1.8%
1.568	.0276	.0270	-2.3%
2.049	.0147	.0143	-2.8%
2.739	$7.08 \times 10^{-3}$	$6.82 \times 10^{-3}$	-3.6%
3.777	$3.00 \times 10^{-3}$	$2.86 \times 10^{-3}$	-4.8%
5.439	$1.07 \times 10^{-3}$	$1.00 \times 10^{-3}$	-6.6%
8.347	$3.01 \times 10^{-4}$	$2.72 \times 10^{-4}$	-9.8%
14.14	$5.91 \times 10^{-5}$	$4.97 \times 10^{-5}$	-15.9%
28.35	$6.33 \times 10^{-6}$	$4.44 \times 10^{-6}$	-29.9%
80.74	$1.96 \times 10^{-7}$	$5.91 \times 10^{-8}$	-69.8%

Table 11

27 Term, Half-Integer Power Basis

Pseudostate Energy $\epsilon$ (a.u.)	$\frac{df}{d\epsilon}$ (Exact)	$\frac{df}{d\epsilon}$ (From Pseudostates after smoothing)	% Error
.0234	1.383	1.371	-.9%
.0681	1.109	1.097	-1.1%
.1286	.843	.832	-1.3%
.2093	.605	.596	-1.4%
.3169	.409	.402	-1.6%
.4615	.258	.253	-1.8%
.6586	.151	.148	-2.1%
.9324	.0818	.0798	-2.5%
1.322	.0403	.0391	-2.9%
1.891	.0178	.0172	-3.4%
2.752	$6.99 \times 10^{-3}$	$6.71 \times 10^{-3}$	-4.1%
4.108	$2.38 \times 10^{-3}$	$2.26 \times 10^{-3}$	-4.9%
6.350	$6.82 \times 10^{-4}$	$6.40 \times 10^{-4}$	-6.0%
10.28	$1.60 \times 10^{-4}$	$1.48 \times 10^{-4}$	-7.6%
17.67	$2.92 \times 10^{-5}$	$2.63 \times 10^{-5}$	-9.7%
32.89	$3.90 \times 10^{-6}$	$3.40 \times 10^{-6}$	-12.8%
68.16	$3.47 \times 10^{-7}$	$2.87 \times 10^{-7}$	-17.2%
163.6	$1.79 \times 10^{-8}$	$1.36 \times 10^{-8}$	-24.0%
485.1	$4.31 \times 10^{-10}$	$2.81 \times 10^{-10}$	-34.8%
$1.983 \times 10^3$	$3.29 \times 10^{-12}$	$1.56 \times 10^{-12}$	-52.4%
$1.404 \times 10^4$	$3.59 \times 10^{-15}$	$8.20 \times 10^{-16}$	-77.1%



Table 12

18 Term, Quarter-Integer Power Basis

Pseudostate Energy $\epsilon$ (a.u.)	$\frac{df}{d\epsilon}$ (Exact)	$\frac{df}{d\epsilon}$ (From Pseudostates after smoothing)	% Error
.0183	1.420	1.353	-4.7%
.1429	.793	.755	-4.8%
.3595	.354	.334	-5.8%
.7421	.124	.115	-7.0%
1.452	.0328	.0300	-8.7%
2.864	$6.30 \times 10^{-3}$	$5.62 \times 10^{-3}$	-10.8%
5.933	$8.32 \times 10^{-4}$	$7.19 \times 10^{-4}$	-13.6%
13.36	$7.07 \times 10^{-5}$	$5.86 \times 10^{-5}$	-17.2%
33.81	$3.56 \times 10^{-6}$	$2.78 \times 10^{-6}$	-21.8%
99.75	$9.62 \times 10^{-8}$	$6.94 \times 10^{-8}$	-27.8%
$3.58 \times 10^2$	$1.23 \times 10^{-9}$	$7.96 \times 10^{-10}$	-35.4%
$1.64 \times 10^3$	$6.38 \times 10^{-12}$	$3.51 \times 10^{-12}$	-44.9%
$1.03 \times 10^4$	$1.07 \times 10^{-14}$	$4.65 \times 10^{-15}$	-56.6%
$9.74 \times 10^4$	$4.13 \times 10^{-18}$	$1.23 \times 10^{-18}$	-70.3%
$1.66 \times 10^6$	$2.03 \times 10^{-22}$	$2.96 \times 10^{-23}$	-85.4%

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## CHAPTER IV

### THE HIGH ENERGY ASYMPTOTIC BEHAVIOR OF THE DIPOLE OSCILLATOR STRENGTH DENSITY AND A NEW "MODIFIED" DIPOLE OSCILLATOR STRENGTH SUM RULE FOR NONRELATIVISTIC N-ELECTRON ATOMS AND MOLECULES

#### A. INTRODUCTION

The high energy asymptotic behavior of the dipole oscillator strength density has been examined for two-electron atoms by Salpeter and Zaidi<sup>1</sup> for use in a Lamb shift calculation of helium and by Dalgarno and Ewart<sup>2</sup> for the photodetachment cross section of the negative hydrogen ion. A Lamb shift calculation by Schwartz<sup>3</sup> was performed using a different approach from that of Salpeter and Zaidi, and the attention was directed toward obtaining  $J(k)$ , a sum over states expression parameterized by  $k$ , the virtual photon energy. The present work shows that the high  $k$  asymptotic expansion of  $J(k)$  given by Schwartz leads to the coefficients of the first two asymptotic terms of the dipole oscillator strength density for any nonrelativistic  $N$ -electron atom in terms of expectation values of the wavefunction. Moreover, an additional term appears in the expansion of  $J(k)$  which is related to the third moment (with respect to the energy) of the oscillator strength distribution with the contributions of the first two asymptotic terms of the oscillator strength density subtracted out beyond some "cut off" value of the energy. This leads to a "sum rule" which gives the third moment of this modified distribution in terms of an expectation value of the wavefunction and the cut off parameter. Note that the third moment of the (unmodified) dipole oscillator strength distribution diverges due to the contributions from the first two asymptotic terms, so the subtraction scheme involving these terms is required in order to obtain finite results. Finally, it is shown that the above results obtained for atoms can be generalized to apply to molecules in the fixed nucleus approximation.

B. THE DIVERGENCE OF S(3) FOR ATOMIC STATES WITH NON-ZERO ONE-ELECTRON DENSITY AT THE NUCLEUS

The familiar oscillator strength sum rules for S(-1), S(0), S(1), and S(2) express moments of the oscillator strength distribution in terms of expectation values of operators for the wavefunction under consideration. It is also straightforward to calculate the operators required to obtain sum rules for S(3), S(4), ... (see e.g. Jackiw<sup>4</sup>) but these are of little interest for atomic ground states since they diverge. The divergence of S(3) for atomic states with non-zero one-electron density at the nucleus is shown in the following. The divergent terms may easily be isolated and the remaining convergent terms will be seen to appear in the sum rule derived in Section D for the modified distribution.

The sum rule for the third moment of the oscillator strength distribution, S(3), may easily be obtained by writing the oscillator strength in the acceleration-acceleration form and one finds

$$S(3) = \sum_n f_{0n} (E_n - E_0)^3 \quad (1)$$

$$= \frac{2}{3} Z^2 \langle \Psi_0 | \sum_{i,j=1}^N \frac{\vec{r}_i \cdot \vec{r}_j}{r_i^3 r_j^3} | \Psi_0 \rangle \quad (2)$$

where  $f_{0n}$  is the oscillator strength between the ground state  $|\Psi_0\rangle$  and the state  $|\Psi_n\rangle$ ,  $E_0$  and  $E_n$  are the energies of  $|\Psi_0\rangle$  and  $|\Psi_n\rangle$  respectively, and  $Z$  is the charge of the nucleus. It is convenient to separate the one-electron terms from the two-electron terms which yields

$$\begin{aligned} S(3) &= \frac{2}{3} Z^2 \langle \Psi_0 | \sum_{i=1}^N \frac{\vec{r}_i \cdot \vec{r}_i}{r_i^6} | \Psi_0 \rangle + \frac{2}{3} Z^2 \langle \Psi_0 | \sum_{i \neq j=1}^N \frac{\vec{r}_i \cdot \vec{r}_j}{r_i^3 r_j^3} | \Psi_0 \rangle \\ &= \frac{2}{3} Z^2 \langle \Psi_0 | \sum_{i=1}^N \frac{1}{r_i^4} | \Psi_0 \rangle + \frac{2}{3} Z^2 \langle \Psi_0 | \sum_{i \neq j=1}^N \frac{\vec{r}_i \cdot \vec{r}_j}{r_i^3 r_j^3} | \Psi_0 \rangle. \end{aligned} \quad (3)$$

The first of the two matrix elements is responsible for the divergence and the second matrix element is well behaved. The first matrix ele-

ment may be expressed in a form where the divergence becomes even more transparent by carrying out two successive integrations by parts. The radial one-electron density shall be defined according to

$$\rho_i(r) = \int d\Omega_i \int d\tau_{\neq i} |\Psi_0|^2, \quad (4)$$

where the integral is performed over the configuration space of all the electrons except that indexed by  $i$ , then an integration is performed over the solid angle associated with electron  $i$ . Then the first matrix element may be written

$$\begin{aligned} & \langle \Psi_0 | \sum_{i=1}^N \frac{1}{r_i^4} | \Psi_0 \rangle \\ &= \sum_{i=1}^N \int_0^\infty \frac{\rho_i(r)}{r^2} dr \\ &= \sum_{i=1}^N \left[ -\frac{\rho_i(r)}{r} \Big|_0^\infty + \ln r \frac{d\rho_i(r)}{dr} \Big|_0^\infty - \int_0^\infty \ln r \frac{d^2\rho_i(r)}{dr^2} dr \right]. \end{aligned} \quad (5)$$

Using the cusp condition,

$$\lim_{r \rightarrow 0} \frac{d\rho_i(r)}{dr} = -2Z \lim_{r \rightarrow 0} \rho_i(r) \quad (6)$$

(due to Kato<sup>5</sup>), allows equation (5) to be rewritten as

$$\begin{aligned} & \langle \Psi_0 | \sum_{i=1}^N \frac{1}{r_i^4} | \Psi_0 \rangle \\ &= \lim_{r \rightarrow 0} \left[ \sum_{i=1}^N \left( \frac{1}{r} + 2Z \ln r \right) \rho_i(r) \right] - \sum_{i=1}^N \int_0^\infty \ln r \frac{d^2\rho_i(r)}{dr^2} \end{aligned} \quad (7)$$

therefore  $S(3)$  is given by

$$\begin{aligned} S(3) &= \frac{2}{3} Z^2 \left[ \lim_{r \rightarrow 0} \sum_{i=1}^N \left( \frac{1}{r} + 2Z \ln r \right) \rho_i(r) \right] \\ &\quad - \frac{2}{3} Z^2 \sum_{i=1}^N \int_0^\infty \ln r \frac{d^2\rho_i(r)}{dr^2} dr \\ &\quad + \frac{2}{3} Z^2 \langle \Psi_0 | \sum_{i \neq j=1}^N \frac{\vec{r}_i \cdot \vec{r}_j}{r_i^3 r_j^3} | \Psi_0 \rangle. \end{aligned} \quad (8)$$



The term in the square brackets clearly yields a divergent result upon evaluation at the limit  $r = 0$  (i.e. at the nucleus). Hence  $S(3)$  diverges for wavefunctions with non-zero one-electron density at the nucleus. The two remaining terms are finite and will appear in the sum rule for the modified distribution to be derived in Section D.

The convergence of  $S(2)$  and the divergence of  $S(3)$  leads to a rather weak result concerning the asymptotic behavior of the oscillator strength distribution, apparently first observed by Dirac and Harding<sup>6</sup>. The fact that the second moment converges and that the third moment does not evidently implies that the oscillator strength density must behave asymptotically as  $df/d\epsilon \propto \epsilon^{-n}$  where  $3 < n \leq 4$ . For atomic states with zero one-electron density at the nucleus (e.g. n-p, n-d, n-f, etc. states of atomic hydrogen)  $S(3)$  is finite, hence  $df/d\epsilon \propto \epsilon^{-n}$  where  $4 < n$ . The disappearance of the asymptotic terms which behave as  $\epsilon^{-n}$  with  $3 < n \leq 4$  for atomic states with zero nuclear one electron density tends to indicate that the coefficients of these terms involve the one-electron density at the nucleus. This suspicion will be confirmed in Section D, which is not surprising since high energy scattering phenomena is frequently highly sensitive to the behavior of the wavefunction at the nucleus.

#### C. DERIVATION OF THE HIGH $k$ ASYMPTOTIC EXPANSION OF $J(k)$

In this section the asymptotic expansion of  $J(k)$  for high values of  $k$  is derived. The derivation essentially follows the presentation by Schwartz<sup>3</sup>, although many additional details are included in this treatment. The first five terms of the asymptotic expansion of  $J(k)$  are obtained with the coefficients determined in terms of expectation values of operators for the wavefunction of interest. Of the five coefficients, the first two reflect well known properties of the oscillator strength distribution, while the last three yield information not previously known (as will be shown in Section D).

The sum over states expression  $J(k)$  is defined by

$$J(k) = \sum_n \frac{K \langle \Psi_n | \vec{\nabla} | \Psi_0 \rangle^2}{E_n - E_0 + k} \quad (9)$$

$$= \frac{3}{2} \sum_n \frac{f_{0n} \omega_{0n}}{\omega_{0n} + k} \quad (10)$$

where

$$\vec{\nabla} = \sum_{i=1}^N \vec{\nabla}_i,$$

$f_{0n}$  is the oscillator strength between state  $|\Psi_0\rangle$  and  $|\Psi_n\rangle$ , and  $\omega_{0n} = E_n - E_0$ . As described in Chapter III,  $J(k)$  may be expressed as

$$J(k) = -\langle \Theta | \vec{\nabla} | \Psi_0 \rangle \quad (11)$$

where  $\Theta = \Theta(r, k)$  is the solution to the inhomogeneous differential equation

$$(H - E_0 + k) |\Theta\rangle + \vec{\nabla} |\Psi_0\rangle = 0. \quad (12)$$

The function  $|\Theta\rangle$  may be formally solved in terms of the complete set of eigenfunctions of  $H$  by

$$|\Theta\rangle = -\sum_n \frac{\langle \Psi_n | \vec{\nabla} | \Psi_0 \rangle}{E_n - E_0 + k} |\Psi_n\rangle. \quad (13)$$

It will prove not only useful, but in fact crucial, to introduce the functional

$$w(\xi, k) = \langle \xi | E_0 - H - k | \xi \rangle - 2 \langle \xi | \vec{\nabla} | \Psi_0 \rangle \quad (14)$$

which is stationary about  $\xi(r, k) = \Theta(r, k)$ , as shown in Chapter III. Note that  $w(\Theta, k) = J(k)$ , so if  $|\Theta\rangle$  is known exactly then either equation (11) or equation (14) may be used to evaluate  $J(k)$ . However if only a close approximation  $|\Theta'\rangle$  to  $|\Theta\rangle$  is known, it is better to use equation (14) and evaluate  $w(\Theta', k)$  rather than  $-\langle \Theta' | \vec{\nabla} | \Psi_0 \rangle$ , since the functional associated with equation (11),  $-\langle \xi | \vec{\nabla} | \Psi_0 \rangle$ ,

will not be stationary about  $\xi = \Theta$ . Inserting a close approximation to  $|\Theta\rangle$  into the stationary functional should lead to a more accurate approximation to  $J(k)$  than using the other expression due to the fact that the first variation of a stationary functional vanishes. Indeed, inserting the approximation to  $|\Theta\rangle$  (which will be obtained below) into the stationary functional gives correct coefficients for the first five terms of the asymptotic expansion, while using the alternate expression yields correct values of only the coefficients of the first three terms. In addition, in this case, use of the stationary functional helps lead to an approximation to  $|\Theta\rangle$  which would appear to be difficult to achieve using other techniques.

The leading term of the asymptotic expansion of  $|\Theta\rangle$  for large  $k$  is clearly seen from equation (12) to be  $-(1/k)\vec{\nabla}|\Psi_0\rangle$ , so  $|\Theta\rangle$  may be written as

$$|\Theta\rangle = -\frac{1}{k}\vec{\nabla}|\Psi_0\rangle + |U\rangle. \quad (15)$$

To proceed further, the Hamiltonian must be specified. Attention shall be restricted to nonrelativistic  $N$ -electron atoms so the Hamiltonian is given by

$$H = \sum_{i=1}^N \left( -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i<j=1}^N \frac{1}{r_{ij}}. \quad (16)$$

Substituting equation (15) into equation (14) then leads to

$$\begin{aligned} w(\Theta, k) &= -\frac{1}{k^2} \langle \Psi_0 | \vec{\nabla} (E_0 - H - k) \vec{\nabla} | \Psi_0 \rangle - \frac{2}{k} \langle \Psi_0 | \nabla^2 | \Psi_0 \rangle \\ &\quad - \frac{2}{k} \langle U | (E_0 - H - k) \vec{\nabla} | \Psi_0 \rangle \\ &\quad + \langle U | (E_0 - H - k) | U \rangle - 2 \langle U | \vec{\nabla} | \Psi_0 \rangle \\ &= -\frac{1}{k} \langle \Psi_0 | \nabla^2 | \Psi_0 \rangle - \frac{1}{k^2} \langle \Psi_0 | \vec{\nabla} [\vec{\nabla}, H] | \Psi_0 \rangle \\ &\quad - \frac{2}{k} \langle U | [\vec{\nabla}, H] | \Psi_0 \rangle + \langle U | (E_0 - H - k) | U \rangle \end{aligned}$$

$$\begin{aligned}
&= -\frac{1}{k} \langle \psi_0 | \nabla^2 | \psi_0 \rangle - \frac{Z}{k^2} \langle \psi_0 | \vec{\nabla} \sum_{i=1}^N \frac{\vec{r}_i}{r_i^3} | \psi_0 \rangle \\
&\quad - \frac{2Z}{k} \langle U | \sum_{i=1}^N \frac{\vec{r}_i}{r_i^3} | \psi_0 \rangle + \langle U | (E_0 - H - k) | U \rangle. \tag{17}
\end{aligned}$$

Note that  $\vec{\nabla}$  is anti-Hermitian and  $\sum \frac{\vec{r}_i}{r_i^3}$  is Hermitian and the reality of the matrix element implies

$$\begin{aligned}
\langle \psi_0 | \vec{\nabla} \sum_{i=1}^N \frac{\vec{r}_i}{r_i^3} | \psi_0 \rangle &= \frac{1}{2} \langle \psi_0 | [\vec{\nabla}, \sum_{i=1}^N \frac{\vec{r}_i}{r_i^3}] | \psi_0 \rangle \\
&= 2\pi \langle \psi_0 | \sum_{i=1}^N \delta(\vec{r}_i) | \psi_0 \rangle. \tag{18}
\end{aligned}$$

Therefore  $w(\Theta, k)$  reduces to

$$\begin{aligned}
w(\Theta, k) &= -\frac{1}{k} \langle \psi_0 | \nabla^2 | \psi_0 \rangle - \frac{2\pi Z}{k^2} \langle \psi_0 | \sum_{i=1}^N \delta(\vec{r}_i) | \psi_0 \rangle \\
&\quad - \frac{2Z}{k} \langle U | \sum_{i=1}^N \frac{\vec{r}_i}{r_i^3} | \psi_0 \rangle + \langle U | (E_0 - H - k) | U \rangle \tag{19}
\end{aligned}$$

$$\begin{aligned}
&= -\frac{1}{k} \langle \psi_0 | \nabla^2 | \psi_0 \rangle - \frac{2\pi Z}{k^2} \langle \psi_0 | \sum_{i=1}^N \delta(\vec{r}_i) | \psi_0 \rangle \\
&\quad + \tilde{w}(U, k) \tag{20}
\end{aligned}$$

where a new functional  $\tilde{w}(\eta, k)$  has been defined by

$$\tilde{w}(\eta, k) = \langle \eta | (E_0 - H - k) | \eta \rangle - \frac{2Z}{k} \langle \eta | \sum_{i=1}^N \frac{\vec{r}_i}{r_i^3} | \psi_0 \rangle. \tag{21}$$

Since  $w(\xi, k)$  was stationary with respect to variations about  $|\xi\rangle = |\Theta\rangle$ , the functional  $\tilde{w}(\eta, k)$  must be stationary with respect to variations about  $|\eta\rangle = |U\rangle$ . This property implies that  $|U\rangle$  satisfies the differential equation

$$(H - E_0 + k) | U \rangle = -\frac{Z}{k} \sum_{i=1}^N \frac{\vec{r}_i}{r_i^3} | \psi_0 \rangle, \tag{22}$$

An approximate solution to  $|U\rangle$  must be constructed such that

the function behaves properly for high  $k$  and small  $\vec{r}_j$ . The importance of the wavefunction near the nucleus for high energy phenomena has already been established and this is essentially why it is necessary for special care to be taken that  $U$  has the correct behavior for small  $\vec{r}_j$ . Before proceeding with the derivation it is necessary to introduce the version of the cusp condition due to Binger<sup>7</sup>, which states that for small  $\vec{r}_j$  and  $|\vec{r}_i| > |\vec{r}_j|$  for all  $i \neq j$

$$\begin{aligned} & \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{j-1}, \vec{r}_j, \vec{r}_{j+1}, \dots, \vec{r}_N) \\ &= \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{j-1}, 0, \vec{r}_{j+1}, \dots, \vec{r}_N) \times [(1 - Zr_j) + \vec{a}_j \cdot \vec{r}_j + \mathcal{O}(r_j^2)] \end{aligned} \quad (23)$$

where

$$\vec{a}_j = \vec{a}_j(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{j-1}, \vec{r}_{j+1}, \dots, \vec{r}_N).$$

The small  $\vec{r}_j$  behavior of  $|\Theta\rangle$  may now be deduced by examining equation (13),

$$|\Theta\rangle = - \sum \frac{\langle \psi_n | \vec{\nabla} | \psi_0 \rangle}{E_n - E_0 + k} |\psi_n\rangle.$$

Evidently the wavefunctions may be expanded according to (if  $|\vec{r}_i| > |\vec{r}_j|$ )

$$\psi_n = \sum_{\nu \ell m} c_{n\nu \ell m}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{j-1}, \vec{r}_{j+1}, \dots, \vec{r}_N) \phi_{\nu \ell}(r_j) Y_{\ell m}(\theta_j, \phi_j) \quad (24)$$

where the elements of  $\{\phi_{\nu 0}(r_j)\}$  (associated with one-electron "S-states") behave as  $1 - Zr_j$  near the nucleus and the elements of  $\{\phi_{\nu 1}(r_j)\}$  (associated with one-electron "P-states") behave as  $r_j$  near the origin. Using equation (23) it is clear that near the origin,  $\vec{\nabla}_j \psi_0$  behaves as

$$\begin{aligned} & \vec{\nabla}_j \psi_0(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{j-1}, \vec{r}_j, \vec{r}_{j+1}, \dots, \vec{r}_N) \\ &= \psi_0(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{j-1}, 0, \vec{r}_{j+1}, \dots, \vec{r}_N) \times \left[ -Z \frac{\vec{r}_j}{r_j} + \vec{a}_{0j} + \mathcal{O}(r_j) \right]. \end{aligned} \quad (25)$$

Note that the correct small  $\vec{r}_j$  behavior of  $\vec{\nabla}_j \Psi_0$  cannot be obtained from an expansion in the basis which describes the  $\Psi_n$  wavefunctions. Each of the three components of

$$-\sum \frac{\vec{r}_j}{r_j^3} \Psi_0(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{j-1}, 0, \vec{r}_{j+1}, \dots, \vec{r}_N)$$

has P symmetry in the jth electron coordinate, yet is nonzero at the nucleus. All the terms in the  $\{\phi_{\nu 1}(r_j)\}$  set behave as  $r_j$ , so use of a finite number  $s$  of these functions to expand a P state which is finite at the nucleus must lead to a function which behaves as  $r_j$  near the nucleus. Taking the limit  $s \rightarrow \infty$  would most likely lead to Gibbs phenomena but it is unnecessary to pursue this any further. Note that the second term in the expansion of  $\vec{\nabla}_j \Psi_0$ ,

$$\vec{a}_{0j} \Psi_0(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{j-1}, 0, \vec{r}_{j+1}, \dots, \vec{r}_N)$$

is also nonzero at the nucleus, but has components with S symmetry, therefore can be obtained from an expansion in terms of the set  $\{\phi_{\nu 0}(r_j)\}$ .

The above observations may now be applied to the expansion of  $|\Theta\rangle$ . Assuming  $k$  is very large, then away from the nucleus it is reasonable to expect

$$\begin{aligned} |\Theta\rangle &\cong -\sum_n \frac{\langle \Psi_n | \vec{\nabla} | \Psi_0 \rangle}{k} |\Psi_n\rangle \\ &\cong -\frac{1}{k} \sum_n |\Psi_n\rangle \langle \Psi_n | \vec{\nabla} | \Psi_0 \rangle. \end{aligned}$$

Hence, away from the nucleus, completeness may be used and

$$|\Theta\rangle \cong -\frac{1}{k} \vec{\nabla} |\Psi_0\rangle$$

which is the first term in the expansion for  $|\Theta\rangle$ , obtained before. However, near the nucleus

$$\begin{aligned}
|\Theta\rangle &= \sum_n \frac{\langle \Psi_n | \sum_i (-z \frac{\vec{r}_i}{r_i} + \vec{a}_{oi} + \vec{\Theta}(r_i)) | \Psi_0 \rangle}{E_n - E_0 + k} |\Psi_n\rangle \\
&\cong -\frac{1}{k} \sum_n |\Psi_n\rangle \langle \Psi_n | \sum_i \vec{a}_{oi} | \Psi_0 \rangle \\
&\quad - \sum_n \frac{\langle \Psi_n | \sum_i (-z \frac{\vec{r}_i}{r_i} + \vec{\Theta}(r_i)) | \Psi_0 \rangle}{E_n - E_0 + k} |\Psi_n\rangle \\
&\cong \left( -\frac{1}{k} \sum_{i=1}^N \vec{a}_{oi} | \Psi_0 \rangle \right) + \sum_{i=1}^N \vec{\Theta}(r_i) \tag{26}
\end{aligned}$$

is the expected behavior from the arguments presented previously. Note that in the summation over  $n$  involving  $\sum_i (\vec{r}_i/r_i)$ , the  $E_n - E_0$  term in the denominator must be retained, since it provides a built in cut off for the high  $E_n$  state contributions. This prevents the occurrence of Gibbs phenomena with associated undefined behavior of  $|\Theta\rangle$  near  $\vec{r}_j = 0$ .

An approximate solution  $|U\rangle$ , to equation (22),

$$(E_0 - H - k)|U\rangle = \frac{z}{k} \sum_i \frac{\vec{r}_i}{r_i^3} |\Psi_0\rangle$$

can now be determined and a homogeneous solution can be chosen which gives  $|\Theta\rangle$  the appropriate behavior near  $\vec{r}_j = 0$ . Writing  $|U\rangle$  as the sum of the particular solution  $|U_1\rangle$  and the homogeneous solution  $|U_2\rangle$ , it is obvious that  $|U_1\rangle = -(z/k^2) \sum_i (\vec{r}_i/r_i^3) |\Psi_0\rangle$  is a valid particular solution for large  $k$  if  $\vec{r}_j$  is not close to the nucleus. However the validity of the solution near the nucleus is necessary and must be checked. The radial component of the Laplacian of a vector expressed in spherical coordinates is required and is given by

$$\begin{aligned}
(\nabla^2 \vec{A})_r &= \nabla^2 A_r - \frac{2A_r}{r^2} - \frac{2}{r^2} \frac{\partial A_\theta}{\partial \theta} \\
&\quad - \frac{2A_\theta \cot \theta}{r^2} - \frac{2}{r^2 \sin \theta} \frac{\partial A_\phi}{\partial \phi} . \tag{27}
\end{aligned}$$

All vector valued functions the Laplacian acts upon in what follows are radial vectors and angle independent (to the order of accuracy desired) so equation (27) becomes

$$(\nabla^2 \vec{A})_r = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial A_r}{\partial r} \right) - \frac{2A_r}{r^2}. \quad (28)$$

For  $|U_1\rangle$  to be a valid particular solution to equation (22) near the nucleus, it is necessary that

$$(E_0 - H) |U_1\rangle = 0 \quad (29)$$

near  $\vec{r}_j = 0$ . Recall that  $|U_1\rangle$  has been assumed to be

$$|U_1\rangle = \vec{V}_1 |\Psi_0\rangle \quad (30)$$

where

$$\vec{V}_1 = \sum_{i=1}^N \vec{V}_{1i} \quad (31)$$

and

$$\vec{V}_{1i} = -\frac{Z}{k^2} \frac{\vec{r}_i}{r_i^3}. \quad (32)$$

Substituting the above form for  $|U_1\rangle$  into equation (29) and then dividing by  $\Psi_0$  leads to the condition on  $\vec{V}_1$  to be verified,

$$\sum_i \left[ \frac{1}{2} \nabla_i^2 + \frac{\vec{\nabla}_i \Psi_0}{\Psi_0} \cdot \vec{\nabla}_i \right] \vec{V}_1 = 0 \quad (33)$$

$\vec{V}_1$  is a sum of one-electron, angle-independent, radial vector valued functions, hence

$$\sum_i \left[ \frac{1}{2} \frac{1}{r_i^2} \frac{\partial}{\partial r_i} \left( r_i^2 \frac{\partial}{\partial r_i} \right) + \frac{\frac{\partial}{\partial r_i} (\Psi_0)}{\Psi_0} \frac{\partial}{\partial r_i} \right] V_{1r} - \frac{1}{2} \sum_i \frac{2}{r_i^2} V_{1r} = 0 \quad (34)$$



where

$$V_{lr} = -\frac{Z}{k^2} \sum_i \frac{1}{r_i^2} \quad (35)$$

and

$$V_{lir} = -\frac{Z}{k^2} \frac{1}{r_i^2} . \quad (36)$$

Near  $\vec{r}_j = 0$ , retaining only the most important terms in the equation yields

$$\left\{ \frac{1}{2} \sum_i \left[ \frac{1}{r_i^2} \frac{\partial}{\partial r_i} \left( r_i^2 \frac{\partial}{\partial r_i} \right) \right] \right\} V_{lr} - \sum_i \frac{1}{r_i^2} V_{lir} = 0 \quad (37)$$

It is easily confirmed that equation (37) is satisfied.

An asymptotic solution  $|U_2\rangle$  (to the homogeneous differential equation) which gives  $|\Theta\rangle$  the correct behavior at the nucleus must now be found. The homogeneous equation is given by

$$(E_0 - H - k) |U_2\rangle = 0 \quad (38)$$

Assume a product solution for  $|U_2\rangle$  of the form  $|U_2\rangle = \vec{V}_2 |\Psi_0\rangle$ . Substituting this expression into equation (38), then dividing by  $\Psi_0$  results in the equation

$$\left\{ \left( \sum_i \left[ \frac{1}{2} \nabla_i^2 + \frac{\vec{\nabla}_i \Psi_0}{\Psi_0} \cdot \vec{\nabla}_i \right] \right) - k \right\} \vec{V}_2 = 0 . \quad (39)$$

Changing variables from  $r$  to  $s = k^{1/2} r$  leads to the equation

$$\left\{ \left( \sum_i \left[ \frac{k}{2} \nabla_{si}^2 + k^{1/2} \left( \frac{\vec{\nabla}_i \Psi_0}{\Psi_0} \right) \cdot \vec{\nabla}_{si} \right] \right) - k \right\} \vec{V}_2 = 0 . \quad (40)$$

Assuming

$$\vec{V}_2 = \vec{V}_2^0 + k^{-1/2} \vec{V}_2^1 + k^{-1} \vec{V}_2^2 + \dots$$

and inserting this form for  $\vec{V}_2$  into the differential equation yields

$$\begin{aligned}
& \left[ \left( \sum_i \frac{1}{2} \nabla_{s_i}^2 \vec{V}_2^0 \right) - \vec{V}_2^0 \right] k \\
& + \left[ \left( \sum_i \frac{1}{2} \nabla_{s_i}^2 \vec{V}_2^1 \right) - \vec{V}_2^1 + \left( \frac{\vec{\nabla}_i \psi_0}{\psi_0} \right) \cdot \vec{\nabla}_{s_i} \vec{V}_2^0 \right] k^{\frac{1}{2}} \\
& + \dots \\
& = 0. \tag{41}
\end{aligned}$$

Equating the coefficients of the powers of  $k$  to zero leads to the system of differential equations

$$\left( \sum_i \frac{1}{2} \nabla_{s_i}^2 \vec{V}_2^0 \right) - \vec{V}_2^0 = 0 \tag{42}$$

$$\left( \sum_i \frac{1}{2} \nabla_{s_i}^2 \vec{V}_2^1 \right) - \vec{V}_2^1 + \left( \frac{\vec{\nabla}_i \psi_0}{\psi_0} \right) \cdot \vec{\nabla}_{s_i} \vec{V}_2^0 = 0 \tag{43}$$

⋮

All that is needed for the present work is the solution to  $\vec{V}_2^0$ . Assuming  $\vec{V}_2^0$  is a sum of one-electron, angle independent, radial vector valued functions, equation (42) may be written as

$$\left\{ \frac{1}{2} \sum_i \left[ \frac{1}{s_i^2} \frac{\partial}{\partial s_i} \left( s_i^2 \frac{\partial}{\partial s_i} \right) \right] - 1 \right\} V_{2r}^0 - \frac{1}{2} \sum_i \frac{2}{s_i^2} V_{2ir}^0 = 0 \tag{44}$$

where  $V_{2r}^0 = \sum_i V_{2ir}^0$ . Since each  $V_{2jr}^0$  has been assumed to be dependent upon only  $s_j$ , the above equation may be separated into solving the equation

$$\left\{ \frac{1}{2} \left( \frac{\partial^2}{\partial s_j^2} \right) + \frac{1}{s_j} \left( \frac{\partial}{\partial s_j} \right) - \frac{1}{s_j^2} - 1 \right\} V_{2jr}^0 = 0 \tag{45}$$

for each  $j = 1, 2, \dots, N$ . This equation has a regular singularity at  $s_j = 0$  and an irregular singularity at  $s_j = \infty$ . The solution (from the indicial equation) near  $s_j = 0$  is easily checked to behave as  $s_j$  or  $s_j^{-2}$ . For large  $s_j$  the solution clearly behaves as

$$e^{\pm \sqrt{2} s_j}.$$

The

$$e^{-\sqrt{2} s_j}$$

choice for large  $s_j$  is required since the homogeneous piece is needed only to correct the solution for small  $r_j$ ; away from the nucleus the solution previously obtained is valid and must not be affected by the homogeneous solution. For small  $s_j$  the  $s_j^{-2}$  behavior must be chosen in order to cancel the  $\sum_i (\bar{r}_i / r_i^3)$  singularity of the particular solution  $|U_1\rangle$ . Writing

$$V_{2jr} = s_j^{-2} e^{-\sqrt{2} s_j} f \quad (46)$$

leads to the differential equation for  $f$  given by

$$\frac{1}{2} f'' + \left(-\frac{1}{s_j} - \sqrt{2}\right) f' + \frac{\sqrt{2}}{s_j} f = 0. \quad (47)$$

Attempting a power series expansion leads to the solution

$$f = c_0 (1 + \sqrt{2} s_j). \quad (48)$$

The other solution to  $f$  (associated with the indicial equation), as expected, goes as  $s_j^3$  for small  $s_j$  and as

$$e^{2\sqrt{2} s_j}$$

for large  $s_j$  and is clearly not wanted. Fortunately for this problem it is not necessary to obtain the second linearly independent solution to  $f$ , which of course will involve logarithmic contributions to the behavior for small  $s_j$ . Therefore the desired solution is given by

$$\vec{V}_2 = c_0 \sum_{i=1}^N \frac{\vec{s}_i}{s_i^3} e^{-\sqrt{2} s_i} (1 + \sqrt{2} s_i) \quad (49)$$

or, in terms of  $\vec{r}_j$ ,

$$\vec{V}_2 = \frac{c_0}{k} \sum_{i=1}^N \frac{\vec{r}_i}{r_i^3} e^{-\mu r_i} (1 + \mu r_i) \quad (50)$$

where  $\mu = (2k)^{1/2}$ . Hence the homogeneous solution is

$$|U_2\rangle = \frac{c_0}{k} \sum_{i=1}^N \frac{\vec{r}_i}{r_i^3} e^{-\mu r_i} (1 + \mu r_i) |\Psi_0\rangle. \quad (51)$$

In order to cancel the singularity associated with the particular solution, the undetermined constant  $c_0$  must be chosen to be  $(Z/k)$ . Thus the desired solution to  $|U\rangle$  is given by

$$|U\rangle = -\frac{Z}{k^2} \sum_{i=1}^N \frac{\vec{r}_i}{r_i^3} [1 - e^{-\mu r_i} (1 + \mu r_i)] |\Psi_0\rangle. \quad (52)$$

Consequently, for small  $r_j$ , the approximation to  $|\Theta\rangle$  behaves as

$$\begin{aligned} |\Theta\rangle &= -\frac{1}{k} \vec{\nabla} |\Psi_0\rangle - \frac{Z}{k^2} \sum_{i=1}^N \frac{\vec{r}_i}{r_i^3} [1 - e^{-\mu r_i} (1 + \mu r_i)] |\Psi_0\rangle \\ &= -\frac{1}{k} \sum_{i=1}^N \left[ -Z \frac{\vec{r}_i}{r_i^3} + \vec{a}_{oi} + \vec{\Theta}(r_i) \right] |\Psi_0\rangle \\ &\quad - \frac{Z}{k^2} \sum_{i=1}^N \frac{\vec{r}_i}{r_i^3} \left[ \frac{\mu^2 r_i^2}{2} + \Theta(r_i^3) \right] |\Psi_0\rangle \\ &= \left( -\frac{1}{k} \sum_{i=1}^N \vec{a}_{oi} |\Psi_0\rangle \right) + \sum_{i=1}^N \vec{\Theta}(r_i) \end{aligned}$$

which is precisely what was needed.

It is appropriate at this point to note that a "cancellation

of errors" has occurred between the approximate particular solution and the approximate homogeneous solution which makes the total solution even better than expected. Recall that in the particular solution the term

$$\sum_i \frac{\frac{\partial}{\partial r_i}(\psi_0)}{\psi_0} \frac{\partial}{\partial r_i} \left( -\frac{Z}{k^2} \frac{1}{r_i^2} \right) = \frac{2Z}{k^2} \sum_i \frac{\frac{\partial}{\partial r_i}(\psi_0)}{\psi_0} \frac{1}{r_i^3}$$

in equation (34) was ignored for small  $r_j$ . Hence the homogeneous equation which was solved afterwards really should have been the inhomogeneous equation

$$\left\{ \left( \sum_i \left[ \frac{1}{2} \nabla_i^2 + \frac{\vec{\nabla}_i \psi_0}{\psi_0} \cdot \vec{\nabla}_i \right] \right) - k \right\} \vec{V}_2 = -\frac{2Z}{k^2} \sum_i \frac{\frac{\partial}{\partial r_i}(\psi_0)}{\psi_0} \frac{\vec{r}_i}{r_i^4}. \quad (53)$$

Now replacing  $V_2$  by the solution which was obtained gives, in the radial component version of equation (53), the "error equality"

$$\sum_i \frac{\frac{\partial}{\partial r_i}(\psi_0)}{\psi_0} \frac{\partial}{\partial r_i} \left[ \frac{Z}{k^2} \frac{e^{-\mu r_i}}{r_i^2} (1 + \mu r_i) \right] = -\frac{2Z}{k^2} \sum_i \frac{\frac{\partial}{\partial r_i}(\psi_0)}{\psi_0} \frac{1}{r_i^3} \quad (54)$$

where the terms on both sides were previously ignored when the homogeneous equation was solved. As can be seen the  $r_j^{-3}$  singularity is canceled, resulting in an even better solution for small  $r_j$  than was realized, because equation (54) is in error for small  $r_j$  to the order of  $r_j^{-2}$ , while the error in the original homogeneous equation was of order  $r_j^{-3}$ .

Having obtained an approximate solution to  $|U\rangle$  with the desired behavior, all that remains is to insert the approximation to  $|U\rangle$  into the functional  $\tilde{W}$  and to evaluate the resulting expression in the limit of large  $k$ , i.e. evaluate

$$\tilde{W}(u, k) = -\frac{2Z}{k} \langle \psi_0 | \sum_{i=1}^N \frac{\vec{r}_i}{r_i^3} | \psi_0 \rangle + \langle u | (E_0 - H - k | u \rangle$$

where

$$|u\rangle = -\frac{Z}{k^2} \sum_{i=1}^N \frac{\vec{r}_i}{r_i^3} [1 - e^{-\mu r_i} (1 + \mu r_i)] | \psi_0 \rangle.$$

The functional  $\tilde{w}(U, k)$  may be written

$$\tilde{w}(U, k) = \tilde{w}_1(U, k) + \tilde{w}_2(U, k) \quad (55)$$

with  $\tilde{w}_1(U, k)$  containing contributions from one-electron operators

$$\tilde{w}_1(U, k) = \sum_{i=1}^N \tilde{w}_{1i}(U, k)$$

where

$$\begin{aligned} & \tilde{w}_{1j}(U, k) \\ &= \frac{2Z^2}{k^3} \langle \Psi_0 | \frac{1}{r_j^4} [1 - e^{-\mu r_j} (1 + \mu r_j)] | \Psi_0 \rangle \\ &+ \frac{Z^2}{k^4} \langle \Psi_0 | \frac{\vec{r}_j}{r_j^3} [1 - e^{-\mu r_j} (1 + \mu r_j)] (E_0 - H - k) \frac{\vec{r}_j}{r_j^3} [1 - e^{-\mu r_j} (1 + \mu r_j)] | \Psi_0 \rangle \end{aligned} \quad (56)$$

and with  $\tilde{w}_2(U, k)$  containing contributions from two-electron operators

$$\begin{aligned} & \tilde{w}_2(U, k) \\ &= \frac{2Z^2}{k^3} \sum_{i \neq j=1}^N \langle \Psi_0 | \frac{\vec{r}_i}{r_i^3} \cdot \frac{\vec{r}_j}{r_j^3} [1 - e^{-\mu r_j} (1 + \mu r_j)] | \Psi_0 \rangle \\ &+ \frac{Z^2}{k^4} \sum_{i \neq j=1}^N \langle \Psi_0 | \frac{\vec{r}_i}{r_i^3} [1 - e^{-\mu r_i} (1 + \mu r_i)] \cdot \\ &\quad \cdot (E_0 - H - k) \frac{\vec{r}_j}{r_j^3} [1 - e^{-\mu r_j} (1 + \mu r_j)] | \Psi_0 \rangle. \end{aligned} \quad (57)$$

The expression  $\tilde{w}_1(U, k)$  shall now be evaluated by determining the contribution from the  $\tilde{w}_{1j}(U, k)$  term. In the following, the indices on the  $r_j$ 's shall be dropped for notational convenience. A straightforward evaluation yields

$$\begin{aligned}
& w_{ij}(u, k) \\
&= \frac{2Z^2}{k^3} \langle \psi_0 | \frac{1}{r^4} [1 - e^{-\mu r(1+\mu r)}] | \psi_0 \rangle \\
&\quad + \frac{Z^2}{k^4} \langle \psi_0 | \frac{\vec{r}}{r^3} [1 - e^{-\mu r(1+\mu r)}] \cdot (E_0 - H - k) \frac{\vec{r}}{r^3} [1 - e^{-\mu r(1+\mu r)}] | \psi_0 \rangle \\
&= \frac{2Z^2}{k^3} \langle \psi_0 | \frac{1}{r^4} [1 - e^{-\mu r(1+\mu r)}] | \psi_0 \rangle \\
&\quad - \frac{Z^2}{k^3} \langle \psi_0 | \frac{1}{r^4} [1 - e^{-\mu r(1+\mu r)}]^2 | \psi_0 \rangle \\
&\quad + \frac{Z^2}{k^4} \langle \psi_0 | \frac{\vec{r}}{r^3} [1 - e^{-\mu r(1+\mu r)}] \cdot (E_0 - H) \frac{\vec{r}}{r^3} [1 - e^{-\mu r(1+\mu r)}] | \psi_0 \rangle \\
&= \frac{2Z^2}{k^3} \langle \psi_0 | \frac{1}{r^4} [1 - e^{-\mu r(1+\mu r)}] | \psi_0 \rangle \\
&\quad - \frac{Z^2}{k^3} \langle \psi_0 | \frac{1}{r^4} [1 - e^{-\mu r(1+\mu r)}]^2 | \psi_0 \rangle \\
&\quad - \frac{Z^2}{k^4} \langle \psi_0 | \frac{\vec{r}}{r^3} [1 - e^{-\mu r(1+\mu r)}] \cdot \frac{\vec{r}}{r^5} [1 - e^{-\mu r(1+\mu r)}] | \psi_0 \rangle \\
&\quad + \frac{Z^2}{k^4} \langle \psi_0 | \frac{1}{r^2} [1 - e^{-\mu r(1+\mu r)}] \frac{1}{2} \{ \nabla^2 (\frac{1}{r^2} [1 - e^{-\mu r(1+\mu r)}]) \} | \psi_0 \rangle \\
&\quad + \frac{Z^2}{k^4} \langle \psi_0 | \frac{1}{r^2} [1 - e^{-\mu r(1+\mu r)}] \{ \vec{\nabla} (\frac{1}{r^2} [1 - e^{-\mu r(1+\mu r)}]) \} \cdot \vec{\nabla} | \psi_0 \rangle \\
&= \frac{2Z^2}{k^3} \langle \psi_0 | \frac{1}{r^4} [1 - e^{-\mu r(1+\mu r)}] | \psi_0 \rangle \\
&\quad - \frac{Z^2}{k^3} \langle \psi_0 | \frac{1}{r^4} [1 - e^{-\mu r(1+\mu r)}]^2 | \psi_0 \rangle \\
&\quad - \frac{Z^2}{k^4} \langle \psi_0 | \frac{\vec{r}}{r^3} [1 - e^{-\mu r(1+\mu r)}] \cdot \frac{\vec{r}}{r^5} [1 - e^{-\mu r(1+\mu r)}] | \psi_0 \rangle \\
&\quad + \frac{Z^2}{k^4} \langle \psi_0 | \frac{\vec{r}}{r^3} [1 - e^{-\mu r(1+\mu r)}] \cdot \frac{\vec{r}}{r^5} [1 - e^{-\mu r(1+\mu r)}] | \psi_0 \rangle
\end{aligned}$$

+ (continued on next page)

$$\begin{aligned}
& - \frac{Z^2}{k^3} \langle \Psi_0 | \frac{\hat{r}}{r^3} [1 - e^{-\mu r} (1 + \mu r)] \cdot \frac{\hat{r}}{r^3} e^{-\mu r} (1 + \mu r) | \Psi_0 \rangle \\
& + \frac{Z}{k^4} \langle \Psi_0 | \frac{1}{r^4} [1 - e^{-\mu r} (1 + \mu r)] \{ r \mu^2 e^{-\mu r} - \frac{2}{r} [1 - e^{-\mu r} (1 + \mu r)] \} \frac{\partial}{\partial r} | \Psi_0 \rangle \quad (58)
\end{aligned}$$

where the angle dependent terms of the Laplacian have been dropped because they lead to terms in  $k$  less significant than the order which will be of interest. Collecting terms results in considerable simplification, yielding

$$\tilde{W}_{ij}(u, k) = \frac{Z^2}{k^3} (A + B) \quad (59)$$

where

$$A = \langle \Psi_0 | \frac{1}{r^4} [1 - e^{-\mu r} (1 + \mu r)] | \Psi_0 \rangle \quad (60)$$

and

$$B = \frac{1}{k} \langle \Psi_0 | \frac{1}{r^4} [1 - e^{-\mu r} (1 + \mu r)] \{ r \mu^2 e^{-\mu r} - \frac{2}{r} [1 - e^{-\mu r} (1 + \mu r)] \} \frac{\partial}{\partial r} | \Psi_0 \rangle. \quad (61)$$

The matrix element  $A$  can easily be written as the integral

$$A = \int_0^\infty \frac{1}{r^2} [1 - e^{-\mu r} (1 + \mu r)] \rho_j(r) dr \quad (62)$$

where as before,

$$\rho_j(r) = \int d\Omega_j \int d\mathbf{v}_{\neq j} |\Psi_0|^2.$$

Note that

$$\frac{d}{dr} \left[ \frac{e^{-\mu r}}{r} - \frac{1}{r} \right] = \frac{1}{r^2} [1 - e^{-\mu r} (1 + \mu r)],$$

hence integration by parts may be applied and, dropping the subscript  $j$  from  $\rho_j(r)$  for notational convenience, it follows that



$$\begin{aligned}
& A \\
& = \left[ \frac{e^{-\mu r}}{r} - \frac{1}{r} \right] \rho(r) \Big|_0^\infty - \int_0^\infty \left[ \frac{e^{-\mu r}}{r} - \frac{1}{r} \right] \frac{d\rho}{dr} dr \\
& = \mu \rho(0) + \int_0^{1/\mu} \left( \frac{1}{r} - \frac{e^{-\mu r}}{r} \right) \frac{d\rho}{dr} dr + \int_{1/\mu}^\infty \left( \frac{1}{r} - \frac{e^{-\mu r}}{r} \right) \frac{d\rho}{dr} dr \\
& = \mu \rho(0) + \int_0^1 \left( \frac{1}{x} - \frac{e^{-x}}{x} \right) \frac{d\rho}{dr} dx \\
& \quad - \int_1^\infty \frac{e^{-x}}{x} \frac{d\rho}{dr} dx + \int_{1/\mu}^\infty \frac{1}{r} \frac{d\rho}{dr} dr \\
& = \mu \rho(0) + \gamma \frac{d\rho}{dr} \Big|_{r=0} - \ln\left(\frac{1}{\mu}\right) \frac{d\rho}{dr} \Big|_{r=0} - \int_{1/\mu}^\infty \ln r \frac{d^2 \rho}{dr^2} dr \\
& \quad + \text{(terms in } k \text{ less significant than } k^0 (= 1)) \\
& = \mu \rho(0) + \gamma \frac{d\rho}{dr} \Big|_{r=0} + \ln \mu \frac{d\rho}{dr} \Big|_{r=0} - \int_0^\infty \ln r \frac{d^2 \rho}{dr^2} dr \\
& \quad + \text{(less significant terms)} \\
& = (2k)^{\frac{1}{2}} \rho(0) + \gamma \frac{d\rho}{dr} \Big|_{r=0} + \frac{1}{2} \ln(2k) \frac{d\rho}{dr} \Big|_{r=0} \\
& \quad - \int_0^\infty \ln r \frac{d^2 \rho}{dr^2} dr + \text{(less significant terms)}. \tag{63}
\end{aligned}$$

Note that above, the Euler-Mascheroni constant,  $\gamma = .57721\dots$  is obtained by applying equation 8.367.12 from the integral tables by Gradshteyn and Ryzhik<sup>8</sup>. Next, the matrix element B may be written as the integral

$$B = \frac{1}{2k} \int_0^\infty \frac{1}{r^2} [1 - e^{-\mu r}(1 + \mu r)] \left\{ r \mu^2 e^{-\mu r} - \frac{2}{r} [1 - e^{-\mu r}(1 + \mu r)] \right\} \frac{d\rho}{dr} dr \tag{64}$$

$$= \alpha + \beta \tag{65}$$

where

$$\alpha = \int_0^{\infty} \frac{e^{-\mu r}}{r} [1 - e^{-\mu r}(1 + \mu r)] \frac{dp}{dr} dr \quad (66)$$

and

$$\beta = -\frac{1}{k} \int_0^{\infty} \frac{1}{r^2} [1 - e^{-\mu r}(1 + \mu r)] \frac{1}{r} [1 - e^{-\mu r}(1 + \mu r)] \frac{dp}{dr} dr. \quad (67)$$

First  $\alpha$  will be expanded:

$$\begin{aligned} \alpha &= \int_0^{\infty} \frac{e^{-\mu r}}{r} [1 - e^{-\mu r}(1 + \mu r)] \frac{dp}{dr} dr \\ &= \int_0^{\infty} \left[ \frac{e^{-\mu r} - e^{-2\mu r}}{r} \right] \frac{dp}{dr} dr - \mu \int_0^{\infty} e^{-2\mu r} \frac{dp}{dr} dr \end{aligned} \quad (68)$$

$$= \ln 2 \left. \frac{dp}{dr} \right|_{r=0} - \frac{1}{2} \left. \frac{dp}{dr} \right|_{r=0} + \left( \begin{array}{l} \text{terms in } k \text{ less} \\ \text{significant than } k^0 \end{array} \right). \quad (69)$$

Note that the first of the two integrals appearing in equation (68) was evaluated using equation 3.434.2 from Gradshteyn and Ryzhik<sup>8</sup>.

Next examine  $\beta$ . Let

$$\beta = \beta_1 + \beta_2 \quad (70)$$

where

$$\beta_1 = -\frac{1}{k} \int_0^{\infty} \frac{1}{r^2} [1 - e^{-\mu r}(1 + \mu r)] \left[ \frac{1}{r} - \frac{e^{-\mu r}}{r} \right] \frac{dp}{dr} dr \quad (71)$$

and

$$\beta_2 = \frac{\mu}{k} \int_0^{\infty} \frac{e^{-\mu r}}{r^2} [1 - e^{-\mu r}(1 + \mu r)] \frac{dp}{dr} dr. \quad (72)$$

The integral  $\beta_1$  may be expanded as follows:

$$\begin{aligned} \beta_1 &= -\frac{1}{k} \int_0^{\infty} \frac{1}{r^2} [1 - e^{-\mu r}(1 + \mu r)] \left[ \frac{1}{r} - \frac{e^{-\mu r}}{r} \right] \frac{dp}{dr} dr \\ &= -\frac{1}{2k} \left[ \frac{1}{r} - \frac{e^{-\mu r}}{r} \right]^2 \frac{dp}{dr} \Big|_0^{\infty} - \frac{1}{2k} \int_0^{\infty} \left[ \frac{1}{r} - \frac{e^{-\mu r}}{r} \right]^2 \frac{d^2 p}{dr^2} dr \\ &= -\left. \frac{dp}{dr} \right|_{r=0} - \frac{1}{2k} \int_0^{\infty} \left[ \frac{1}{r} - \frac{e^{-\mu r}}{r} \right]^2 \frac{d^2 p}{dr^2} dr \end{aligned}$$

$$= -\left. \frac{d\rho}{dr} \right|_{r=0} + (\text{terms in } k \text{ less significant than } k^0) \quad (73)$$

Next,  $\beta_2$  may be expanded:

$$\begin{aligned} \beta_2 &= \frac{\mu}{k} \int_0^\infty \frac{e^{-\mu r}}{r^2} [1 - e^{-\mu r}(1 + \mu r)] \frac{d\rho}{dr} dr \\ &= \frac{\mu}{k} \left[ \frac{e^{-\mu r}}{r} - \frac{1}{r} \right] e^{-\mu r} \frac{d\rho}{dr} \Big|_0^\infty \\ &\quad - \frac{\mu}{k} \int_0^\infty \left[ \frac{e^{-\mu r}}{r} - \frac{1}{r} \right] \left( -\mu e^{-\mu r} \frac{d\rho}{dr} + e^{-\mu r} \frac{d^2\rho}{dr^2} \right) dr \\ &= 2 \left. \frac{d\rho}{dr} \right|_{r=0} - 2 \ln 2 \left. \frac{d\rho}{dr} \right|_{r=0} + (\text{terms in } k \text{ less significant than } k^0). \quad (74) \end{aligned}$$

Finally, the asymptotic expansion of  $\tilde{w}(U, k)$  is obtained by summing the integrals

$$\begin{aligned} \tilde{w}_{ij}(U, k) &= \frac{Z^2}{k^3} [A + \alpha + \beta_1 + \beta_2] \\ &= \frac{Z^2}{k^3} \left[ (2k)^{\frac{1}{2}} \rho_j(0) + \frac{1}{2} \ln k \left. \frac{d\rho_j}{dr} \right|_{r=0} - \frac{1}{2} \ln 2 \left. \frac{d\rho_j}{dr} \right|_{r=0} \right. \\ &\quad \left. + \frac{1}{2} \left. \frac{d\rho_j}{dr} \right|_{r=0} + \gamma \left. \frac{d\rho_j}{dr} \right|_{r=0} - \int_0^\infty \ln r \frac{d^2\rho_j}{dr^2} dr \right. \\ &\quad \left. + (\text{terms in } k \text{ less significant than } k^0) \right]. \quad (75) \end{aligned}$$

The cusp condition allows one to eliminate  $\left. \frac{d\rho_j}{dr} \right|_{r=0}$  because

$$\left. \frac{d\rho_j}{dr} \right|_{r=0} = -2Z\rho_j(0),$$

hence,

$$\begin{aligned} \tilde{w}_{ij}(U, k) = & \frac{Z^2}{k^3} \rho_j(0) \left[ (2k)^{\frac{1}{2}} - Z \ln k + Z(\ln 2 - 1 - 2\delta) \right] \\ & - \frac{Z^2}{k^3} \int_0^\infty \ln r \frac{d^2 \rho_j}{dr^2} dr + \left( \begin{array}{l} \text{terms in } k \text{ less} \\ \text{significant than } k^0 \end{array} \right). \end{aligned} \quad (76)$$

Therefore, to order  $k^{-3}$ ,  $\tilde{w}_1(U, k)$  is given by

$$\begin{aligned} \tilde{w}_1(U, k) = & \frac{Z^2}{k^3} \sum_{i=1}^N \left\{ \rho_i(0) \left[ (2k)^{\frac{1}{2}} - Z \ln k + Z(\ln 2 - 1 - 2\delta) \right] \right. \\ & \left. - \int_0^\infty \ln r \frac{d^2 \rho_i}{dr^2} dr \right\}. \end{aligned} \quad (77)$$

Equation (77) may be further simplified by noting that for an anti-symmetric wavefunction  $\Psi_0$  in the defining equation (4) for the one-electron density it follows that

$$\rho_1(r) = \rho_2(r) = \dots = \rho_N(r) = \rho(r),$$

hence

$$\begin{aligned} \tilde{w}_1(U, k) = & \frac{Z^2}{k^3} N \left\{ \rho(0) \left[ (2k)^{\frac{1}{2}} - Z \ln k + Z(\ln 2 - 1 - 2\delta) \right] \right. \\ & \left. - \int_0^\infty \ln r \frac{d^2 \rho}{dr^2} dr \right\}. \end{aligned} \quad (78)$$

Fortunately the task of computing  $\tilde{w}_2(U, k)$  is much simpler. The terms which contribute to the order in  $k$  of interest are simply

$$\begin{aligned} \tilde{w}_2(U, k) = & \frac{2Z^2}{k^3} \sum_{i \neq j=1}^N \langle \Psi_0 | \frac{\vec{r}_i}{r_i^3} \cdot \frac{\vec{r}_j}{r_j^3} | \Psi_0 \rangle \\ & + \frac{Z^2}{k^4} \sum_{i \neq j=1}^N \langle \Psi_0 | \frac{\vec{r}_i}{r_i^3} \cdot (-k) \frac{\vec{r}_j}{r_j^3} | \Psi_0 \rangle \\ = & \frac{Z^2}{k^3} \sum_{i \neq j=1}^N \langle \Psi_0 | \frac{\vec{r}_i}{r_i^3} \cdot \frac{\vec{r}_j}{r_j^3} | \Psi_0 \rangle. \end{aligned} \quad (79)$$

Therefore, adding  $\tilde{w}_1(U, k)$  and  $\tilde{w}_2(U, k)$  gives  $\tilde{w}(U, k)$  with

$$\begin{aligned}
& \tilde{w}(U, k) \\
&= \frac{Z^2}{k^3} N \left\{ \rho(0) \left[ (2k)^{\frac{1}{2}} - Z \ln k + Z (\ln 2 - 1 - 2\delta) \right] \right. \\
&\quad \left. - \int_0^\infty \ln r \frac{d^2 \rho}{dr} dr \right\} \\
&+ \frac{Z^2}{k^3} \sum_{i \neq j=1}^N \langle \Psi_0 | \frac{\vec{r}_i}{r_i^3} \cdot \frac{\vec{r}_j}{r_j^3} | \Psi_0 \rangle. \tag{80}
\end{aligned}$$

Substituting this expansion for  $\tilde{w}$  into the expansion previously obtained for  $w$  leads to the final result for  $J(k)$ ,

$$\begin{aligned}
& J(k) \\
&= -\frac{1}{k} \langle \Psi_0 | \nabla^2 | \Psi_0 \rangle - \frac{2\pi Z}{k^2} \langle \Psi_0 | \sum_{i=1}^N \delta(\vec{r}_i) | \Psi_0 \rangle \\
&+ \frac{Z^2}{k^3} (2k)^{\frac{1}{2}} N \rho(0) - \frac{Z^3}{k^3} \ln k N \rho(0) \\
&+ \frac{Z^2}{k^3} \left\{ Z (\ln 2 - 1 - 2\delta) N \rho(0) - N \int_0^\infty \ln r \frac{d^2 \rho}{dr^2} dr \right. \\
&\quad \left. + \sum_{i \neq j=1}^N \langle \Psi_0 | \frac{\vec{r}_i}{r_i^3} \cdot \frac{\vec{r}_j}{r_j^3} | \Psi_0 \rangle \right\} \tag{81}
\end{aligned}$$

valid to order  $k^{-3}$  in  $k$ .

#### D. THE EXPANSION OF $J(k)$ IN TERMS OF THE MOMENTS AND ASYMPTOTIC BEHAVIOR OF THE OSCILLATOR STRENGTH DISTRIBUTION

In this section it is shown that the form of the sum over states expression  $J(k)$  allows an expansion in  $k$  with coefficients given in terms of global (i.e. moment) and asymptotic properties of the oscillator strength distribution. The expansion is similar in spirit to the Cauchy expansion of the dynamic polarizability which

yields a power series in the frequency, with coefficients given in terms of the negative even moments of the oscillator strength distribution. The coefficients in the expansion of  $J(k)$  obtained in this section (in terms of properties of the oscillator strength distribution) may then be identified with those obtained in the previous section (which were obtained as expectation values of the wavefunction). The identification immediately leads to "sum rules" for the coefficients of the first and second asymptotic terms of the oscillator strength density, along with the third moment of a "modified" oscillator strength distribution.

The sum over states expression  $J(k)$  has been defined in equation (10) to be

$$J(k) = \frac{3}{2} \sum_n \frac{f_{on}(\epsilon_n - \epsilon_0)}{\epsilon_n - \epsilon_0 + k}$$

where the sum ranges over the bound discrete states and implies integration over the continuum of scattering states. The above summation may be split into 1)  $\sum'$ , a summation over all the bound states with an implicit integration up to some energy  $b$  in the continuum, and 2)  $\int_b^\infty d\epsilon$ , an integration over the continuum from  $\epsilon = b$  to  $\infty$ . Then the above equation may be written as

$$J(k) = \frac{3}{2} \sum'_n \frac{f_{on}(\epsilon_n - \epsilon_0)}{\epsilon_n - \epsilon_0 + k} + \frac{3}{2} \int_b^\infty \frac{df}{d\epsilon} \frac{(\epsilon - \epsilon_0)}{(\epsilon - \epsilon_0 + k)} d\epsilon. \quad (82)$$

An asymptotic expansion in  $k$  is now desired for large  $k$ . This can be achieved if  $b$  is chosen such that  $b \ll k$  over the range of interest of  $k$ . Assuming  $b \ll k$ , it is found (following the same method used for the Cauchy expansion of the dynamic polarizability) that

$$\sum'_n \frac{f_{on}(\epsilon_n - \epsilon_0)}{\epsilon_n - \epsilon_0 + k} = \frac{S'(1,b)}{k} - \frac{S'(2,b)}{k^2} + \frac{S'(3,b)}{k^3} + \dots \quad (83)$$

where  $S'(i,b)$  denotes the  $i$ -th moment of the portion of the oscil-

lator strength distribution below energy  $b$ .

An expansion for the integral is also required. This may be accomplished by repeated partial integrations. In the following, as before,  $b$  is taken such that  $b < k$ . Also, it shall be assumed that asymptotically the oscillator strength behaves as

$$\frac{df}{d\epsilon} = \alpha \epsilon^{-7/2} + \beta \epsilon^{-4} + \left( \begin{array}{l} \text{terms which fall} \\ \text{off faster than } \epsilon^{-4} \end{array} \right). \quad (84)$$

This choice for the asymptotic behavior is consistent with Dirac and Harding's observation and it is of the same form as obtained for atomic hydrogen (as shown in Section E of Chapter III) and atomic helium<sup>1</sup>. After completing the following derivation it will become obvious that this is the only choice for the first two asymptotic terms which will yield terms in the expansion of  $J(k)$  of the same form as that obtained in the previous section. Note that in the following,  $S''(i,b)$  will denote the  $i$ -th moment of the portion of the oscillator strength distribution above energy  $b$ . Carrying out the partial integrations,

$$\begin{aligned} & \int_b^{\infty} \frac{df}{d\epsilon} \frac{(\epsilon - \epsilon_0)}{(\epsilon - \epsilon_0 + k)} d\epsilon \\ &= \left( - \int_{\epsilon}^{\infty} \frac{df}{d\epsilon'} (\epsilon' - \epsilon_0) d\epsilon' \right) \frac{1}{(\epsilon - \epsilon_0 + k)} \Big|_b^{\infty} - \int_b^{\infty} \left( \int_{\epsilon}^{\infty} \frac{df}{d\epsilon'} (\epsilon' - \epsilon_0) d\epsilon' \right) \frac{1}{(\epsilon - \epsilon_0 + k)^2} d\epsilon \\ &= \frac{S''(1,b)}{(b - \epsilon_0 + k)} - \int_b^{\infty} \left( \int_{\epsilon}^{\infty} \frac{df}{d\epsilon'} (\epsilon' - \epsilon_0) d\epsilon' \right) \frac{1}{(\epsilon - \epsilon_0 + k)^2} d\epsilon \\ &= \frac{S''(1,b)}{(b - \epsilon_0 + k)} - \left\{ \left( \int_{\epsilon}^{\infty} \frac{df}{d\epsilon'} (\epsilon' - \epsilon_0) d\epsilon' \right) \frac{\epsilon - \epsilon_0}{(\epsilon - \epsilon_0 + k)^2} \Big|_b^{\infty} \right\} \\ & \quad - \int_b^{\infty} \left\{ \frac{df}{d\epsilon} \frac{(\epsilon - \epsilon_0)}{(\epsilon - \epsilon_0 + k)^2} + 2 \left( \int_{\epsilon}^{\infty} \frac{df}{d\epsilon'} (\epsilon' - \epsilon_0) d\epsilon' \right) \frac{1}{(\epsilon - \epsilon_0 + k)^3} \right\} (\epsilon - \epsilon_0) d\epsilon \end{aligned}$$

$$\begin{aligned}
&= \frac{S''(1,b)}{(b-\epsilon_0+k)} + \frac{S''(1,b)}{(b-\epsilon_0+k)^2} (b-\epsilon_0) \\
&+ \int_b^\infty \left\{ \frac{df}{d\epsilon} \frac{(\epsilon-\epsilon_0)^2}{(\epsilon-\epsilon_0+k)^2} - 2 \left( \int_\epsilon^\infty \frac{df}{d\epsilon'} (\epsilon'-\epsilon_0) d\epsilon' \right) \frac{(\epsilon-\epsilon_0)}{(\epsilon-\epsilon_0+k)^3} \right\} d\epsilon \\
&= \frac{S''(1,b)}{(k+b-\epsilon_0)} + \frac{S''(1,b)}{(k+b-\epsilon_0)^2} (b-\epsilon_0) - \frac{S''(2,b)}{(k+b-\epsilon_0)^2} \\
&- 2 \frac{S''(2,b)}{(k+b-\epsilon_0)^3} (b-\epsilon_0) + 2 \frac{S''(1,b)}{(k+b-\epsilon_0)^3} (b-\epsilon_0)^2 \\
&+ \int_b^\infty \frac{df}{d\epsilon} \frac{(\epsilon-\epsilon_0)^3}{(\epsilon-\epsilon_0+k)^3} d\epsilon + 6 \int_b^\infty \left( \int_\epsilon^\infty \frac{df}{d\epsilon'} (\epsilon'-\epsilon_0)^2 d\epsilon' \right) \frac{(\epsilon-\epsilon_0)}{(\epsilon-\epsilon_0+k)^4} d\epsilon \\
&- 3 \int_b^\infty \left( \int_\epsilon^\infty \frac{df}{d\epsilon'} (\epsilon'-\epsilon_0) d\epsilon' \right) \frac{(\epsilon-\epsilon_0)^2}{(\epsilon-\epsilon_0+k)^4} d\epsilon . \tag{85}
\end{aligned}$$

At this stage, the above expression may be reduced by noting that to order  $k^{-3}$  the sum of the first five terms in equation (85) is equal to

$$\frac{S''(1,b)}{k} - \frac{S''(2,b)}{k^2} .$$

So, to order  $k^{-3}$ ,

$$\begin{aligned}
&\int_b^\infty \frac{df}{d\epsilon} \frac{(\epsilon-\epsilon_0)}{(\epsilon-\epsilon_0+k)} d\epsilon \\
&= \frac{S''(1,b)}{k} - \frac{S''(2,b)}{k^2} + \int_b^\infty \frac{df}{d\epsilon} \frac{(\epsilon-\epsilon_0)^3}{(\epsilon-\epsilon_0+k)^3} d\epsilon \\
&+ 6 \int_b^\infty \left( \int_\epsilon^\infty \frac{df}{d\epsilon'} (\epsilon'-\epsilon_0)^2 d\epsilon' \right) \frac{(\epsilon-\epsilon_0)}{(\epsilon-\epsilon_0+k)^4} d\epsilon \\
&- 3 \int_b^\infty \left( \int_\epsilon^\infty \frac{df}{d\epsilon'} (\epsilon'-\epsilon_0) d\epsilon' \right) \frac{(\epsilon-\epsilon_0)^2}{(\epsilon-\epsilon_0+k)^4} d\epsilon . \tag{86}
\end{aligned}$$



The three integrals appearing on the right hand side of equation (86) must now be dealt with. The standard procedure cannot be used because asymptotically

$$\frac{df}{d\epsilon} = \alpha \epsilon^{-7/2} + \beta \epsilon^{-4} + \dots,$$

so the usual technique would lead to a divergence on the boundary at  $\infty$ . However, define

$$\left(\frac{df}{d\epsilon}\right)^* = \frac{df}{d\epsilon} - \alpha \epsilon^{-7/2} - \beta \epsilon^{-4} \quad (87)$$

and one finds

$$\begin{aligned} & \int_b^\infty \left[ \frac{df}{d\epsilon} \frac{(\epsilon - \epsilon_0)^3}{(\epsilon - \epsilon_0 + k)^3} + 6 \left( \int_\epsilon^\infty \frac{df}{d\epsilon'} (\epsilon' - \epsilon_0)^2 d\epsilon' \right) \frac{(\epsilon - \epsilon_0)}{(\epsilon - \epsilon_0 + k)^4} \right. \\ & \quad \left. - 3 \left( \int_\epsilon^\infty \frac{df}{d\epsilon'} (\epsilon' - \epsilon_0) d\epsilon' \right) \frac{(\epsilon - \epsilon_0)^2}{(\epsilon - \epsilon_0 + k)^4} \right] d\epsilon \\ &= \frac{S^{*''}(3, b)}{k^3} + \int_b^\infty (\alpha \epsilon^{-7/2} + \beta \epsilon^{-4}) \frac{(\epsilon - \epsilon_0)^3}{(\epsilon - \epsilon_0 + k)^3} d\epsilon \\ & \quad + \int_b^\infty \left\{ 6 \left[ \int_\epsilon^\infty (\alpha \epsilon'^{-7/2} + \beta \epsilon'^{-4}) (\epsilon' - \epsilon_0)^2 d\epsilon' \right] \frac{(\epsilon - \epsilon_0)}{(\epsilon - \epsilon_0 + k)^4} \right. \\ & \quad \left. - 3 \left[ \int_\epsilon^\infty (\alpha \epsilon'^{-7/2} + \beta \epsilon'^{-4}) (\epsilon' - \epsilon_0) d\epsilon' \right] \frac{(\epsilon - \epsilon_0)^2}{(\epsilon - \epsilon_0 + k)^4} \right\} d\epsilon \\ & \quad + (\text{terms of higher order than } k^{-3}) \end{aligned} \quad (88)$$

where

$$S^{*''}(3, b) = \int_b^\infty \left(\frac{df}{d\epsilon}\right)^* (\epsilon - \epsilon_0)^3 d\epsilon. \quad (89)$$

Now, only the remaining three integrals on the right hand side of equation (88) need be evaluated. These integrals may be performed

analytically and upon expansion to order  $k^{-3}$  it is found that

$$\begin{aligned} & \int_b^{\infty} (\alpha \epsilon^{-7/2} + \beta \epsilon^{-4}) \frac{(\epsilon - \epsilon_0)^3}{(\epsilon - \epsilon_0 + k)^3} d\epsilon \\ &= \frac{1}{k^3} \left[ -2\alpha b^{1/2} + \frac{3\pi}{8} \alpha k^{1/2} - 6\alpha \epsilon_0 b^{-1/2} + 2\alpha \epsilon_0^2 b^{-3/2} - \frac{2}{5} \alpha \epsilon_0^3 b^{-5/2} \right. \\ & \quad \left. - \frac{3}{2} \beta + \beta \ln k - \beta \ln b - 3\beta \epsilon_0 b^{-1} + \frac{3}{2} \beta \epsilon_0^2 b^{-2} - \frac{\beta}{3} \epsilon_0^3 b^{-3} \right] \\ & \quad + (\text{higher order terms}), \end{aligned} \quad (90)$$

$$\begin{aligned} & 6 \int_b^{\infty} \left[ \int_{\epsilon}^{\infty} (\alpha \epsilon'^{-7/2} + \beta \epsilon'^{-4}) (\epsilon' - \epsilon_0)^2 d\epsilon' \right] \frac{(\epsilon - \epsilon_0)}{(\epsilon - \epsilon_0 + k)^4} d\epsilon \\ &= \frac{1}{k^3} \left[ \frac{3\pi}{4} \alpha k^{1/2} + 2\beta \right] + (\text{higher order terms}) \end{aligned} \quad (91)$$

and

$$\begin{aligned} & -3 \int_b^{\infty} \left[ \int_{\epsilon}^{\infty} (\alpha \epsilon'^{-7/2} + \beta \epsilon'^{-4}) (\epsilon' - \epsilon_0) d\epsilon' \right] \frac{(\epsilon - \epsilon_0)^2}{(\epsilon - \epsilon_0 + k)^4} d\epsilon \\ &= \frac{1}{k^3} \left[ -\frac{\pi}{8} \alpha k^{1/2} - \frac{\beta}{2} \right] + (\text{higher order terms}). \end{aligned} \quad (92)$$

Combining all the above results it is found that, to order  $k^{-3}$ ,

$$\begin{aligned} & \sum_n \frac{f_{0n}(\epsilon_n - \epsilon_0)}{(\epsilon_n - \epsilon_0 + k)} \\ &= \frac{S'(1,b)}{k} + \frac{S''(1,b)}{k} - \frac{S'(2,b)}{k^2} - \frac{S''(2,b)}{k^2} + \frac{S'(3,b)}{k^3} + \frac{S^*(3,b)}{k^3} \\ & \quad + \alpha \pi \frac{k^{1/2}}{k^3} + \beta \frac{\ln k}{k^3} \end{aligned}$$

+ (continued on next page)

$$+ \frac{1}{k^3} \left[ -2\alpha b^{1/2} - 6\alpha \epsilon_0 b^{-1/2} + 2\alpha \epsilon_0^2 b^{-3/2} - \frac{2}{5}\alpha \epsilon_0^3 b^{-5/2} \right. \\ \left. - \beta \ln b - 3\beta \epsilon_0 b^{-1} + \frac{3}{2}\beta \epsilon_0^2 b^{-2} - \frac{1}{3}\beta \epsilon_0^3 b^{-3} \right]. \quad (93)$$

Noting that  $S'(i,b) + S''(i,b) = S(i)$  leads to the further simplification that

$$\sum_n \frac{f_{on} (\epsilon_n - \epsilon_0)}{(\epsilon_n - \epsilon_0 + k)} \\ = \frac{S(1)}{k} - \frac{S(2)}{k^2} + \alpha \pi \frac{k^{1/2}}{k^3} + \beta \frac{\ln k}{k^3} + \frac{c}{k^3} + \left( \begin{array}{l} \text{higher} \\ \text{order terms} \end{array} \right) \quad (94)$$

where

$$c = S'(3,b) + S^{*''}(3,b) \\ - 2\alpha b^{1/2} - 6\alpha \epsilon_0 b^{-1/2} + 2\alpha \epsilon_0^2 b^{-3/2} - \frac{2}{5}\alpha \epsilon_0^3 b^{-5/2} \\ - \beta \ln b - 3\beta \epsilon_0 b^{-1} + \frac{3}{2}\beta \epsilon_0^2 b^{-2} - \frac{1}{3}\beta \epsilon_0^3 b^{-3}. \quad (95)$$

It is easily verified that  $c$  is a constant independent of  $b$ , as it must be, since  $b$  was only artificially introduced to perform the evaluation. Note that  $S'(3,b) + S^{*''}(3,b)$  is the third moment of a modified oscillator strength distribution where the

$$\alpha \epsilon^{-7/2} + \beta \epsilon^{-4}$$

contribution to  $(df/d\epsilon)$  has been subtracted above the energy  $b$ , i.e.

$$S'(3,b) + S^{*''}(3,b) = \sum_n f_{on} \omega_{on}^3 \\ + \int_{\epsilon_I}^0 \frac{df}{d\epsilon} (\epsilon - \epsilon_0)^3 d\epsilon \\ + \int_0^\infty \left\{ \frac{df}{d\epsilon} - \Theta(\epsilon - b) [\alpha \epsilon^{-7/2} + \beta \epsilon^{-4}] \right\} (\epsilon - \epsilon_0)^3 d\epsilon \quad (96)$$

where  $\epsilon_I$  is the first ionization threshold and  $\Theta$  is the unit step

function. Also note  $J(k)$  is given to order  $k^{-3}$  by

$$J(k) = \frac{3}{2} \frac{S(1)}{k} - \frac{3}{2} \frac{S(2)}{k^2} + \frac{3}{2} \alpha \pi \frac{k^{1/2}}{k^3} + \frac{3}{2} \beta \frac{\ln k}{k^3} + \frac{3}{2} \frac{c}{k^3} \quad (97)$$

with  $c$  given as above.

Equating the coefficients of the above  $J(k)$  with that obtained in Section C automatically gives the final results,

$$S(1) = -\frac{2}{3} \langle \Psi_0 | \nabla^2 | \Psi_0 \rangle \quad (98)$$

$$S(2) = \frac{4\pi Z}{3} \langle \Psi_0 | \sum_{i=1}^N \delta(\vec{r}_i) | \Psi_0 \rangle = \frac{Z}{3} N\rho(0) \quad (99)$$

$$\alpha = \frac{2}{3} \frac{Z^2 \sqrt{2}}{\pi} N\rho(0) = \frac{2\sqrt{2} Z}{\pi} S(2) \quad (100)$$

$$\beta = -\frac{2}{3} Z^3 N\rho(0) = -2Z^2 S(2) \quad (101)$$

and

$$\begin{aligned} & S'(3,b) + S^{*''}(3,b) \\ &= \sum_n f_{on} \omega_{on}^3 + \int_{\epsilon_1}^0 \frac{df}{d\epsilon} (\epsilon - \epsilon_0)^3 d\epsilon \\ & \quad + \int_0^\infty \left\{ \frac{df}{d\epsilon} - \Theta(\epsilon-b) [\alpha \epsilon^{-7/2} + \beta \epsilon^{-4}] \right\} (\epsilon - \epsilon_0)^3 d\epsilon \\ &= \frac{4}{3} Z^3 N\rho(0) \left[ \frac{1}{2} \ln 2 - \frac{1}{2} - .5772 \dots \right] \\ & \quad + \frac{2}{3} Z^2 \left[ \sum_{i \neq j=1}^N \langle \Psi_0 | \frac{\vec{r}_i \cdot \vec{r}_j}{r_i^3 r_j^3} | \Psi_0 \rangle - N \int_0^\infty \ln r \frac{d^2 \rho}{dr^2} dr \right] \\ & \quad + 2\alpha b^{1/2} + 6\alpha \epsilon_0 b^{-1/2} - 2\alpha \epsilon_0^2 b^{-3/2} + \frac{2}{5} \alpha \epsilon_0^3 b^{-5/2} \\ & \quad + \beta \ln b + 3\beta \epsilon_0 b^{-1} - \frac{3}{2} \beta \epsilon_0^2 b^{-2} + \frac{1}{3} \beta \epsilon_0^3 b^{-3} \end{aligned} \quad (102)$$

where all quantities are expressed in atomic units. Of the above five results, the first two are well known from the usual sum rules. The third and fourth identities give the coefficients of the first two

terms in the asymptotic expansion of the oscillator strength density and are in agreement with results obtained by Salpeter and Zaidi<sup>1</sup> for atomic helium. Finally, the fifth result is a sum rule for the third moment of the modified distribution.

#### E. RESULTS FOR MOLECULES

The previous results obtained for atoms are easily extended to apply to nonrelativistic N-electron molecules in the fixed nucleus approximation. In this case the Hamiltonian is given by

$$H = \sum_{i=1}^N \left( -\frac{\nabla_i^2}{2} - \sum_{\mu=1}^M \frac{Z_{\mu}}{r_{\mu i}} \right) + \sum_{i < j} \frac{1}{r_{ij}} \quad (103)$$

where  $\mu$  ranges over the M nuclei of the molecule and  $r_{\mu i}$  denotes the distance between the  $\mu$ th nucleus (with charge  $Z_{\mu}$ ) and the  $i$ -th electron. For this Hamiltonian the length, velocity and acceleration forms of the dipole operator are given by  $\vec{L}$ ,  $\vec{V}$  and  $\vec{A}$  respectively, where

$$\vec{L} = \sum_{i=1}^N \vec{r}_i \quad (104)$$

$$\vec{V} = [\vec{L}, H] = \sum_{i=1}^N \vec{\nabla}_i \quad (105)$$

$$\vec{A} = [\vec{V}, H] = \sum_{\mu=1}^M Z_{\mu} \sum_{i=1}^N \frac{\vec{r}_{\mu i}}{r_{\mu i}^3} \quad (106)$$

with  $\vec{r}_{\mu i} = (\vec{r}_i - \vec{r}_{\mu})$ .

The acceleration form of the dipole operator A given above for molecules, of course, differs from that used in the derivation of the expansion of J(k) for atoms. Making the necessary replacements for  $\vec{A}$  and H is quite straightforward and the net effect is the appearance of the index  $\mu$  (which labels the nuclei) and the associated summation. Note that the cusp condition applies to both atoms and mole-

cules so the arguments previously made for atoms may be easily extended to deal with molecules. The final results obtained are given by

$$S(1) = -\frac{2}{3} \langle \psi_0 | \nabla^2 | \psi_0 \rangle \quad (107)$$

$$S(2) = \frac{4\pi}{3} \sum_{\mu=1}^M Z_{\mu} \langle \psi_0 | \sum_{i=1}^N \delta(\vec{r}_{\mu i}) | \psi_0 \rangle \quad (108)$$

$$= \frac{1}{3} \sum_{\mu=1}^M Z_{\mu} \sum_{i=1}^N \rho_{\mu i}(0) \quad (109)$$

$$\alpha = \frac{2\sqrt{2}}{3\pi} \sum_{\mu=1}^M Z_{\mu}^2 \sum_{i=1}^N \rho_{\mu i}(0) \quad (110)$$

$$\beta = -\frac{2}{3} \sum_{\mu=1}^M Z_{\mu}^3 \sum_{i=1}^N \rho_{\mu i}(0) \quad (111)$$

and

$$\begin{aligned} & S'(3, b) + S^{*''}(3, b) \\ &= \frac{4}{3} \sum_{\mu=1}^M Z_{\mu}^3 \sum_{i=1}^N \rho_{\mu i}(0) \left[ \frac{1}{2} \ln 2 - \frac{1}{2} - .5772 \dots \right] \\ &+ \frac{2}{3} \left[ \left( \sum_{\substack{(M, N) \\ (\mu, i) \neq (v, j) = (1, 1)}} Z_{\mu} Z_{\nu} \langle \psi_0 | \frac{\vec{r}_{\mu i} \cdot \vec{r}_{\nu j}}{r_{\mu i}^3 r_{\nu j}^3} | \psi_0 \rangle \right) \right. \\ &\quad \left. - \left( \sum_{\mu=1}^M Z_{\mu}^2 \sum_{i=1}^N \int_0^{\infty} \ln r \frac{d^2 \rho_{\mu i}}{dr^2} dr \right) \right] \\ &+ 2\alpha b^{1/2} + 6\alpha \epsilon_0 b^{-1/2} - 2\alpha \epsilon_0^2 b^{-3/2} + \frac{2}{5} \alpha \epsilon_0^3 b^{-5/2} \\ &+ \beta \ln b + 3\beta \epsilon_0 b^{-1} - \frac{3}{2} \beta \epsilon_0^2 b^{-2} + \frac{1}{3} \beta \epsilon_0^3 b^{-3} \end{aligned} \quad (112)$$

where  $\rho_{\mu i}(r)$  in the above is defined by

$$\rho_{\mu i}(r) = \int d\Omega_{\mu i} \int d\tau_{\neq i} |\psi_0|^2 \quad (113)$$

with the "μi" angular integration carried out about the point  $\vec{r}_{\mu}$  and r denotes the separation from the point  $\vec{r}_{\mu}$ .

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## CHAPTER V

### THE APPLICATION OF WAVEFUNCTION EXPECTATION VALUES TOWARD THE CALCULATION OF LOGARITHMIC MEAN EXCITATION ENERGIES AND THE HIGH ENERGY PHOTOIONIZATION CROSS SECTION FOR ATOMS AND MOLECULES

#### A. INTRODUCTION

Various attempts have been made in the past to utilize information from sum rules and knowledge of the asymptotic form of the oscillator strength density for calculations of atomic properties. Dalgarno and Lynn<sup>1</sup> modified available theoretical values of oscillator strengths of atomic helium to satisfy sum rules, while assuming a functional form for the oscillator strength density with a reasonable asymptotic behavior. They then employed the new values to evaluate various properties of helium arising from second order perturbation theory. Dalgarno and Stewart<sup>2</sup> followed a similar procedure to calculate the Lamb shift of helium, with improved values of oscillator strengths and the correct coefficient of the first asymptotic term of the oscillator strength density. Garcia<sup>3</sup> has suggested an approximate analytic representation of the oscillator strength sum,  $S(k)$ , which can be fit to a set of values (at  $k = 2, 1, 0, -1, -2, -4, -6$ ) known from sum rules and experiment. Garcia's representation of  $S(k)$  is consistent with the asymptotic form of the oscillator strength density and can be used to obtain estimates of the Bethe logarithm required for the evaluation of the Lamb shift.

The present work describes the construction of an effective oscillator strength distribution, which satisfies not only the usual sum rules, but also has the correct asymptotic behavior and satisfies the "modified" oscillator strength sum rule described in Chapter IV of this work. The functional form assumed for the effective distribution consists of discrete states plus a continuous density extending from infinity down to some cut off value of the energy.



The constants required to specify the effective distribution are obtained by solving a system of nonlinear algebraic equations. In Chapter II, which described the solution of a similar system of equations, a rather remarkable simplification reduced the problem to one of finding the roots of a polynomial. No such dramatic simplifications occur here, and the approach used to solve the equations is the multi-dimensional generalization of the Newton-Raphson method. Once the effective distribution has been obtained, it is a simple matter to obtain estimates for the logarithmic mean excitation energies and the photoionization cross section. Finally, calculations have been performed for atomic hydrogen using the effective distribution and are compared with exact results.

#### B. THE EFFECTIVE DISTRIBUTION AND ITS MOMENTS

The effective oscillator strength distribution is assumed to consist of a set of  $M$  discrete states and a continuous density. The  $m$ -th discrete state is completely determined by specifying the oscillator strength  $f'_m$  and the associated energy difference (with the ground state)  $\omega'_m$ . The effective oscillator strength density is of the form

$$\frac{df'}{d\epsilon} = \alpha (\epsilon - \epsilon_0)^{-7/2} + \beta (\epsilon - \epsilon_0)^{-4} + \gamma (\epsilon - \epsilon_0)^{-9/2} \quad (1)$$

(where  $\epsilon_0$  is the ground state energy), and extends from infinity down to some cut off energy  $\epsilon = b$ . Clearly the  $k$ -th moment with respect to the ground state energy  $\epsilon_0$  of this distribution is given by

$$S'(k) = \sum_{n=1}^M f'_n \omega'_n{}^k + \frac{\alpha}{\frac{5}{2} - k} (b - \epsilon_0)^{k-5/2} + \frac{\beta}{3-k} (b - \epsilon_0)^{k-3} + \frac{\gamma}{\frac{7}{2} - k} (b - \epsilon_0)^{k-7/2}. \quad (2)$$

For atoms, the  $\alpha$  and  $\beta$  are chosen to be

$$\alpha = \frac{2}{3} \frac{Z^2 \sqrt{2}}{\pi} N \rho(0) \quad (3)$$

and

$$\beta = -\frac{2}{3} Z^3 N \rho(0) \quad (4)$$

where  $Z$  is the nuclear charge,  $N$  is the number of electrons and  $\rho(0)$  is the one-electron density at the nucleus. For molecules, the corresponding expressions obtained in Section E of Chapter IV must be used. With this choice of  $\alpha$  and  $\beta$ , the effective oscillator strength density correctly assumes the first two asymptotic terms of the actual oscillator strength density, as shown in Chapter IV.

For the continuum oscillator strength density, which lies above the first ionization threshold energy  $\epsilon_I$ , it shall prove necessary to introduce a modified oscillator strength density of the form

$$\tilde{\frac{df}{d\epsilon}} = \frac{df}{d\epsilon} - \Theta(\epsilon-b) [\alpha(\epsilon-\epsilon_0)^{-7/2} + \beta(\epsilon-\epsilon_0)^{-4}] \quad (5)$$

where  $\Theta$  is the unit step function and  $b$  is some cut off energy lying between  $\epsilon_I$  and  $\infty$ . Then  $\tilde{S}(k,b)$ , the  $k$ -th moment of the modified oscillator strength distribution consisting of the (unmodified) discrete states plus the modified density above  $\epsilon_I$ , is given by

$$\begin{aligned} & \tilde{S}(k,b) \\ &= \sum_n f_{on} \omega_{on}^k \\ &+ \int_{\epsilon_I}^{\infty} \left\{ \frac{df}{d\epsilon} - \Theta(\epsilon-b) [\alpha(\epsilon-\epsilon_0)^{-7/2} + \beta(\epsilon-\epsilon_0)^{-4}] \right\} (\epsilon-\epsilon_0)^k d\epsilon. \quad (6) \end{aligned}$$

It is easily verified that  $\tilde{S}(k,b)$  is related to  $S(k)$ , the  $k$ -th moment of the oscillator strength distribution, through the equation

$$\tilde{S}(k,b) = S(k) - \frac{\alpha}{\frac{5}{2}-k} (b-\epsilon_0)^{k-5/2} - \frac{\beta}{3-k} (b-\epsilon_0)^{k-3}. \quad (7)$$

The basic approach to be followed here is to fit the  $S'(k)$  (defined in equation (2)) to a set of known  $S(k)$ . However, it is known from the derivation given in Chapter IV that the third moment of the "modified" distribution is also known. The procedure described here allows the effective distribution to satisfy the usual moments known from sum rules and, in addition, allows the "modified" effective distribution to satisfy the value of the third moment of the actual "modified" oscillator strength distribution. Note that  $S(k)$  is infinite for  $k = 3$ , however  $\tilde{S}(3,b)$  is well defined, and from the results presented in Chapter IV it is possible to show that

$$\tilde{S}(3,b) = S_f(3) + 2\alpha(b-\epsilon_0)^{\frac{1}{2}} + \beta \ln(b-\epsilon_0) \quad (8)$$

where  $S_f(3)$ , the "finite" part of  $S(3)$ , is given for atoms by

$$S_f(3) = \frac{4}{3} Z^3 N \rho(0) \left[ \frac{1}{2} \ln 2 - \frac{1}{2} - C_{EM} \right] + \frac{2}{3} Z^2 \left[ \sum_{i \neq j=1}^N \langle \psi_0 | \frac{\vec{r}_i \cdot \vec{r}_j}{r_i^3 r_j^3} | \psi_0 \rangle - N \int_0^\infty \ln r \frac{d^2 \rho}{dr^2} dr \right] \quad (9)$$

with  $C_{EM} = .5772\dots$ , the Euler-Mascheroni constant. For molecules  $S_f(3)$  is given by the generalization easily obtained from the results presented in Section E of Chapter IV.

The effective oscillator strength distribution described above contains the unknown parameters  $\gamma$ ,  $b$ , and  $f'_n$  and  $\omega'_n$  for  $n = 1, 2, \dots, M$ . These  $2M + 2$  unknown constants shall be determined by requiring that  $2M + 2$  of the moments of the effective distribution are equal to those of the actual oscillator strength distribution (known from sum rules, experiment, variational calculations, etc.). Of the resulting  $2M + 2$  equations, one of these equates the third moment of the modified oscillator strength distribution to the third moment of the corresponding modified effective distribution. More precisely, it shall be required that the effective distribution satisfy

$$\tilde{S}(k,b) = \sum_{n=1}^M f'_n \omega'_n{}^k + \frac{\gamma}{\frac{7}{2} - k} (b - \epsilon_0)^{k - 7/2} \quad (10)$$