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SUM RULES FOR VARIATIONAL WAVE FUNCTIONS

by

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ABSTRACT

Conditions are given under which a variationally determined frequency dependent polarizability will satisfy the oscillator strength sum rule.

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In their variational calculations of the frequency dependent dipole polarizability of helium, Chan and Dalgarno[1] found that their approximate oscillator strengths automatically satisfied the oscillator strength sum rule whatever the size of the basis set they used. In the first part of this note we exhibit the underlying reason for this result,[2] and in the second part we will generalize the result to situations involving non linear variational parameters. We will use the notation of reference 1 throughout, except that instead of considering the dipole polarizability we will consider an arbitrary polarizability. Hence we replace their $\underline{r}$ by V .

Expansion of the trial function $\chi_t(\omega)$ in terms of a fixed basis set is readily seen[3] to be equivalent to finding the exact polarizability of a system described by a Hamiltonian $\bar{H}$ under a perturbation $\bar{V}$ where the bar denotes projection onto the basis set plus ψ_o.[4] Thus, by the usual argument the sum of the approximate oscillator strengths will satisfy

$$\sum g_\ell = \frac{1}{2}\left(\psi_0, \left[\bar{V}, [\bar{H}, \bar{V}]\right] \psi_0\right)$$

where the square bracket denotes a commutator. We will now show that if $V\psi_0$ is a member of the basis set (as was the case in the work reported in reference 1) then

$$\left(\psi_0, \left[\bar{V}, [\bar{H}, \bar{V}]\right]\psi_0\right) = \left(\psi_0, \left[V, [H, V]\right]\psi_0\right) \quad (1)$$

which of course then explains the result found in reference 1.

The proof is simple[6], we merely look at the two sorts of terms involved. First consider $I_1 = (\psi_0, \bar{V} \bar{H} \bar{V} \psi_0)$ Since $V\psi_0$ is in the basis set we have $\bar{V} \psi_0 = V\psi_0$ whence $I_1 = (\psi_0, V \bar{H} V \psi_0)$ which in turn, for the same reason, equals $(\psi_0, V H V \psi_0)$. Finally consider $I_2 = (\psi_0, \bar{V} \bar{V} \bar{H} \psi_0)$ This can be written successively as $I_2 = E_0 (\psi_0, \bar{V} \bar{V} \psi_0) = E_0 (\psi_0, V V \psi_0) = (\psi_0, V V H \psi_0)$. Equation (1) then clearly f follows from these results.[7]

We now turn to a more general situation. If one uses non-linear variational parameters then the whole concept of an oscillator strength will probably be meaningless (it will depend on ω). However one may still ask, does one have

$$\lim_{\omega \to \infty} \alpha(\omega) = \frac{1}{2} \frac{(\psi_0, [V, [H, V]] \psi_0)}{\omega^2} \quad ?$$

We will now show that if one gets the frequency dependence correct that then the coefficient will be correct provided (as was the case above)

$$\delta \chi_t = V \psi_0$$

is an allowed variation.

In accord with this assumption let us assume that our trial functions can be written as

$$\chi_t = \alpha V \psi_0 + \beta X$$

where α and β are variational parameters and where X can be "anything". For convenience but without loss of generality we will however assume that

$$(V\psi_0, X) = 0$$

Further, in accord with our assumptions we will assume that as $\omega \to \infty$ the optimal trial function takes the form

$$\chi_t \to \frac{A}{\omega} + \frac{B}{\omega^2} + \cdots \qquad (2)$$

Indeed this is probably not really an assumption since the analysis below implies that for consistency, the already assumed form of the trial function plus the variation principle, pretty much implies (2). The proof now proceeds as follows: Evidently $\delta\chi_t = \chi_t$ is an allowed variation whence it follows from the variation principle

$$(\delta\chi_t, (H - E_0 + \omega)\chi_t) + (\delta\chi_t, V\psi_0) = 0$$

that the optimal value of the polarizability will be

$$\alpha = \frac{1}{2}\left[(V\psi_0, \chi_t(\omega)) + (V\psi_0, \chi_t(-\omega))\right] \qquad (3)$$

Suppose now that we vary only α. Then we have that

$$(V\psi_0, (H - E_0 + \omega)\chi_t) + (V\psi_0, V\psi_0) = 0$$

Then letting $\omega \to \infty$ and using (2) one finds from the terms independent of ω that

$$(V\psi_0, A) + (V\psi_0, V\psi_0) = 0 \tag{4}$$

while from the terms of order ω^{-1} one finds

$$(V\psi_0, (H-E_0) A) + (V\psi_0, B) = 0 \tag{5}$$

Thus from (4) and (5) we have that as $\omega \to \infty$

$$(V\psi_0, \chi_t) \to -\frac{(V\psi_0, V\psi_0)}{\omega} - \frac{(\psi_0, [H,V] A)}{\omega^2} \tag{6}$$

We will now show that $A = -V\psi_0$. Then (6), in conjunction with (3), will yield the announced result since

$$(\psi_0, [V, [H,V]]\psi_0) = 2\,(\psi_0, [H,V]\,V\psi_0)$$

To show that $A = -V\psi_0$ we note that from (4) it follows that

$$A = -V\psi_0 + A_\perp$$

where $(V\psi_0, A_\perp) = 0$, and further it is clear that $A_\perp$ can only arise from X , i.e., as $\omega \to \infty$, χ must go to a constant times $\frac{A_\perp}{\omega}$. Now let us vary β . Then we learn from the variational principle that

$$(X, (H - E + \omega) \psi_+) = 0$$

which, in the infinite frequency limit, yields

$$(A_\perp, A) = 0$$

or

$$(A_\perp, A_\perp) = 0 \quad \therefore \quad A_\perp = 0$$

which proves the point.

Footnotes and References

1. Y. M. Chan and A. Dalgarno, Proc. Phys. Soc., <u>86</u>, (777) (1965).
2. Similar conclusions have been reached by A. Dalgarno and G. A. Victor (A. Dalgarno, private communication).
3. See for example H. J. Kolker and H. H. Michels, J. Chem. Phys., 43, 1027 (1965).
4. We will assume that ψ_0 is exact, that is that $H\psi_0 = \bar{H}\psi_0 = E_0\psi_0$ However our results still apply to the calculations in reference 1 since although their ψ_0 is not the exact ground state eigenfunction for He, their method of calculation in effect replaced the exact helium Hamiltonian by another such that $H\psi_0 = E_0\psi_0$ is satisfied.(5) Since further this Hamiltonian involves only a local potential, the dipole oscillator strength sum rule is unchanged.
5. They put $\chi_t = F\psi_0$ and wrote $(H-E_0)\chi_t = [T,F]\psi_0$ where T is the kinetic energy operator. Thus they effectively replaced the helium Hamiltonian by the Sternheimer Hamiltonian, R. M. Sternheimer, Phys. Rev. 96, 951 (1954).
6. For a related result see R. E. Johnson et al, J. Chem. Phys. <u>47</u>, 1271 (1967), footnote 8.
7. In connection with the discussion in Footnotes 5 and 6 we may note that if $H\psi_0 \neq E_0\psi_0$ then one readily finds that the left hand side of (1) equals the right hand side of (1) plus $(\psi_0, (H-\mathcal{H})V^2\psi_0) + (\psi_0, V^2(H-\mathcal{H})\psi_0)$ where $\mathcal{H}\psi_0 = E_0\psi_0$. Note that the discrepancy is independent of the size of the basis set.