Conditions for zeros in the generalized oscillator strength: One-electron atom and diatomic molecule examples

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Requirements for the existence of isolated zeros in the generalized oscillator strength (GOS) for one-electron atoms and molecules are considered. It is shown that in certain limits the atomic GOS cannot be zero for any value of the momentum-transfer magnitude $\hbar K \neq 0$ unless it is zero for all values. A relationship between the existence of a zero and the angular momentum of the target's states is pointed out for the atomic case and a numerical example is provided. The conditions for the existence of an isolated zero for a molecular GOS are derived and, using the atom case as a model, they indicate that one is unlikely for $0 < K < \infty$ and the internuclear separation R restricted to $0 < R < \infty$. Minima, or possibly zeros, in the molecular GOS occur in both experiment and theory. It is postulated here that these structures are minima and not zeros. They appear to be due to zeros in a matrix element related to the leading term of the small-K GOS expansion while higher terms remain finite. Several numerical examples are provided and the speculation is supported by the correlation of the GOS minimum as a function of K and R to a zero in the dipole oscillator strength. Attention is brought to the existence of zeros in the molecular dipole oscillator strength when a nodeless function appears in this matrix element, contrary to the atomic case, and an explanation for this difference is given.

I. INTRODUCTION

The predictions of isolated zeros in the dipole oscillator strength (DOS) and generalized oscillator strength (GOS), and their implications with respect to observation, have been of interest for many years. One of the most discussed examples[1] is the zeros in the photoionization cross section for atoms, which are termed Cooper minima.[2] This idea has been extended to include transitions between discrete states.[3] The recent literature contains advances in the mathematical characterization of these structures as well as many numerical examples. See Ref. 4 and its citations.

The situation is similar for the GOS function where the isolated zero for a given transition occurs as a function of the magnitude of the momentum transfer $\hbar K$. Their importance has long been recognized.[5] Theoretical[5-11] and experimental[12,13] GOS zeros for atoms have been studied. In the case of molecules, theoretical[14-16] and experimental[14,17-19] examples are also available. The verification of a GOS zero in the associated electron scattering experiment is difficult because of accuracy loss in measuring a necessarily small cross section. However, observed nonzero minima are often associated with theoretical zeros[20] and in one case the experimental GOS for a molecule H_2O is compatible with the existence of an isolated zero.[18] The term minimum implies a nonzero minimum in the following discussion.

The present study of zeros in the GOS starts with a consideration of atomic transitions. The main result achieved here is to quantify the role of the target's initial and final electronic state's orbital angular momentum quantum number L. The published examples show that most, if not all, zeros are associated with transitions involving an ns with $n > 1$ orbital, although minima may still appear[6] when this condition is not satisfied. Continuum-state transitions, when summed over all partial-L cross sections, appear to have only minima.[9]

A proof is presented that identifies conditions for which the GOS must be zero for all K if it is zero for any value of K. This proof systematizes many of the observations made in the above paragraph and shows that the essential parameter for a discrete transition is $\min(L_f, L_i)$ where i and f indicate the initial, final target electronic states and $\min(\ )$ is equal to the smallest number contained in the parentheses. A numerical example in the spirit of Ref. 6 will be used to show why zeros for the $\min(L_f, L_i) = 1$ case are not common and why no example appears to exist for the $\min(L_f, L_i) = 2$ case.

Equations for the existence of an isolated zero in the GOS for a one-electron diatomic molecule at some K and R, where R is the internuclear separation, are presented. They require an infinite number of two-dimensional matrix elements to vanish. A proof that these equations make the existence of an isolated zero impossible was not found but, by analogy with the atom case, one is unlikely. These equations express in a mathematical form the point made in the discussion on the last page of Ref. 14 where it is stated that the GOS may vanish for a particular orientation of the molecule, but it will probably not be zero for all orientations.

It is postulated on the basis of these results that a

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molecular GOS cannot have an isolated zero for $0 < K < \infty$ and $0 < R < \infty$. The observed structures in theory[14-16] and experiment[14,17-19] are minima and, like the minima seen in the atom case,[6] are due to the vanishing of just one of a number of matrix elements that appear in the GOS expression. The speculative nature of these statements must be emphasized, especially since one experiment[18] measured a GOS for which a local zero is within the error limits. Consequently, a proof or negation of these speculations is required to clarify the present situation.

The first of the infinite number of matrix elements that must vanish for the existence of an isolated zero in the molecule case becomes proportional to the dipole matrix element as K becomes small. Since this is expected to be the largest term for small K in a dipole-allowed transition, the vanishing of this matrix element would have the most effect on the shape of the GOS. Also, if this is the responsible term, the minima in the GOS must correlate as a function of K and R to a zero in the DOS. Several numerical examples of this behavior for H_2^+ dipole-allowed transitions are presented. The individual matrix elements are investigated for one case and the leading term has an isolated zero that correlates like the GOS minimum while higher terms remain finite.

Similar data exist for all transitions discussed in Ref. 21 and it is interesting to note that no dipole-forbidden transition for all R in that list shows the structure found in earlier publications[15,16] and here for the dipole-allowed transitions. The small undulatory behavior observable in some of the data shown here is not the subject of the present discussion. These secondary features have been explained[22] as interference between the two atomic centers for the homopolar molecule and, if seen, occur for $KR \geq 2$. The final example shown here is for a dipole-allowed transition that has isolated zeros in the DOS for $R = 0$ and $R \simeq 5.5a_0$. The GOS structure associated with the $R \simeq 5.5a_0$ zero is evident and is similar to the other examples. The structure found for the $R = 0$ DOS zero is quite different and is dominated by multiple zeros in a higher term. This latter behavior seems not to have been previously reported.

This raises the question of zeros in the molecule DOS. In the H_2^+ case the dipole matrix element for $R = 0$ and $R \to \infty$ are two different hydrogenic matrix elements,

with differing nuclear charges, determined by the H_2^+ correlation diagram. The established fact[23] that the hydrogenic DOS matrix elements cannot vanish requires that they all have the same sign. Since the sign of the hydrogenic matrix elements does not change as a function of nuclear charge, the conclusion that only an even number of zeros can occur for a given molecular DOS and $0 < R < \infty$ seems safe. This argument is faulty, as shown below, and many examples of an odd number of zeros are known.[24,25] Of equal interest and partly as a consequence of the situation just described is the occurrence of zeros in the DOS for a molecular transition involving a nodeless function. This is unlike the atom case, for which it appears[26] that no zeros are known for this type of transition.

Most of the theoretical treatments cited above and the present analysis employ a one-electron model for the target's electronic structure. Also, the presentation is strictly nonrelativistic. The generalization of both the atom and molecule results to cases requiring the Pauli approximation is a matter of notation. The present analysis does not apply to the Dirac equation. Hence any reference to experiment ignores complexities due to many-electron and certain relativistic effects.

II. ATOMIC TARGETS

The GOS is too familiar to present in any detail beyond that required to define the terms to be discussed. Following Ref. 6, the target wave functions for the atom case are taken as discrete states defined by

$$\psi(\mathbf{r};Z) = P_{NL}(r;Z)Y_{LM}(\hat{\mathbf{r}}) , \tag{1}$$

where Y_{LM} is a spherical harmonic and P_{NL} is some radial orbital. P_{NL} is a hydrogenic orbital with an effective nuclear charge Z in Ref. 6 and this approximation is used without loss of generality in the present context. The standard definition for the quantum numbers N, L, and M is assumed. If the expansion

$$e^{i\mathbf{K}\cdot\mathbf{r}} = 4\pi \sum_{l,m} i^l j_l(Kr) Y_{lm}^*(\hat{\mathbf{K}}) Y_{lm}(\hat{\mathbf{r}}) \tag{2}$$

is used, the generalized oscillator strength is related to the Born matrix element $\varepsilon(K)$ and is proportional to

$$|\varepsilon(K)|^2/K^2 \equiv (1/4\pi K^2) \int d\Omega(\hat{\mathbf{n}}) \left| \int d\mathbf{r}\, \psi_f^*(\mathbf{r};Z_f) e^{i\mathbf{K}\cdot\mathbf{r}} \psi_i(\mathbf{r};Z_i) \right|^2$$

$$= K^{-2} \sum_{l=0}^{\infty} |G(L_i,L_f,l;M_f,M_i)a_{l,\alpha-1/2}|^2 , \tag{3}$$

where $N_i \neq N_f$, the only nonzero terms must satisfy the Clebsch-Gordan triangle relationship,

$$|L_f - L_i| \leq 2l + \alpha \leq L_f + L_i ,$$

$$\alpha = \begin{cases} 0, & L_i + L_f \text{ even} \\ 1, & L_i + L_f \text{ odd} , \end{cases}$$

and

$$a_{l,\alpha-1/2} \equiv \int_0^{\infty} r^2 dr\, P_{N_f L_f}(r;Z_f) P_{N_i L_i}(r;Z_i) j_{2l+\alpha}(Kr) . \tag{4}$$

The solid-angle $d\Omega(\hat{\mathbf{n}})$ integral is over all angles between $\mathbf{K}$ and the quantization axis for the target atom. The constant G contains the expected[6] Clebsch-Gordan coefficients plus other constants not needed here and

$G \neq 0$ for the l values discussed following Eq. (3). This development is given in more detail by Ref. 6 where it is shown that the GOS, defined by Eq. (3), depends on the two parameters K/Z_i and Z_f/Z_i, where Z_i and Z_f are the effective nuclear charges for the initial and final states.

The special nature of the $K = 0$ point can be seen by examining the $K \to 0$ limit of Eqs. (3) and (4). Under the stated conditions, all but the $l = 0$ and $\alpha = 1$ term in Eq. (3) vanishes in this limit. This remaining term contains the well-known[18] relationship between the DOS and the $K = 0$ limit of the GOS.

Each term of the sum in Eq. (3) must vanish if a local zero exists in the GOS at some K and this in turn requires the integral defined by Eq. (4) to equal zero for this K and each l satisfying the triangle relationship. One integral must vanish if $\min(L_f, L_i) = 0$. [In general, $\min(L_f, L_i) + 1$ matrix elements must vanish.] This represents one transcendental equation in two unknowns and any solutions that may exist will be curves or points in the $K/Z_i - Z_f/Z_i$ plane if the Ref. 6 parametrization is used. These solutions are easier to locate by working with Eq. (4), which changes sign near the zero, than with Eq. (3) or the GOS.

Two integrals must vanish if $\min(L_f, L_i) = 1$ and the GOS can only vanish at the points of intersection for the corresponding solution curves. An example is shown in Fig. 1 where two vanishing points for the GOS were found. The search shown in Fig. 1 was not restricted to be representative of a known physical system. In the same vein, three curves must intersect at the same point if $\min(L_f, L_i) = 2$. This presents an ill-posed problem for the present model since there are only two adjustable parameters. However, it would be a simple matter to con-
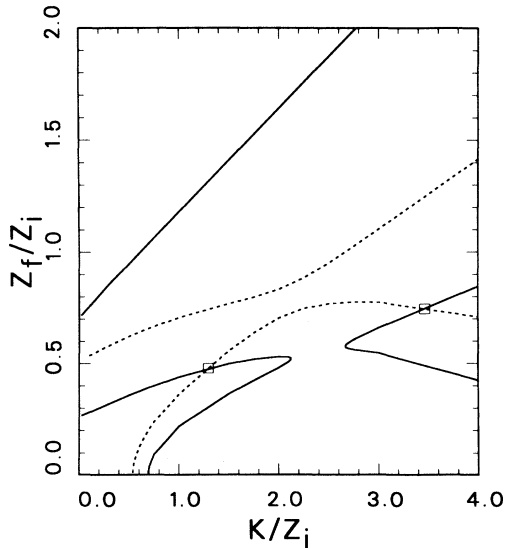
struct a model with three parameters, etc.

It is interesting to note that no examples of GSO zeros appear to have been published for the $\min(L_f, L_i) = 2$ case. The above discussion makes it clear that such a zero could be found but the added constraints imposed by the system being modeled have, to date, excluded this possibility.

The circumstances for which the increase in $\min(L_f, L_i)$ cannot be continued indefinitely and still display a local zero in the GOS are now pointed out. If $\min(L_f, L_i) \to \infty$ such that $|L_f - L_i| = \alpha$, the product $P_{N_f L_f} P_{N_i L_i}$ must be a trivial function (zero for all r) if the GOS is presumed to vanish for any point with $K \neq 0$.

The proof starts by noting that the Eq. (4) matrix element must equal zero for $0 \leq l < \infty$ if the given conditions on L_f and L_i are satisfied and if Eq. (3) equals zero for some $0 < K < \infty$. The formal expansion

$$f(x) = \sum_{l=0}^{\infty} (2\alpha + 1 + 4l) J_{2l+\alpha+1/2}(x)$$
$$\times \int_0^{\infty} dt\, t^{-1} f(t) J_{2l+\alpha+1/2}(t)$$
$$= \sum_{l=0}^{\infty} (2\alpha + 1 + 4l) J_{2l+\alpha+1/2}(x) a_{l,\alpha-1/2} \qquad (5)$$

can be written, where

$$f(x) \equiv \sqrt{(\pi x/2)} x^2 K^{-3} P_{N_f L_f}(x/K; Z_f) P_{N_i L_i}(x/K; Z_i) , \qquad (6)$$

and $a_{l,\alpha-1/2}$ is defined by Eq. (4). If certain continuity and integrability conditions are satisfied, Wilkins[27] has shown that the above Neumann series converges to $f(x)$. These conditions are satisfied for the cases under consideration. Since $a_{l,\alpha-1/2} = 0$ for all l and $f(x) = 0$ for all $0 \leq x < \infty$, Eq. (6) requires the product of radial orbitals to be zero if $0 < K < \infty$. This can only be true if the product of radial orbitals is zero for all allowed r or, in other words, if the GOS is equal to zero for one K value it must vanish for all K in the allowed range.

A continuum transition can be treated as a series of discrete transitions, one for each partial wave. In this case $0 \leq L_f < \infty$, so the condition $\min(L_f, L_i) \to \infty$ with $|L_f - L_i| = \alpha$ reduces to considering a partial wave in the $L_i \to \infty$ limit. The above proof requires this partial wave to be identically zero if the GOS vanishes for any $K > 0$. All partial waves must be trivially zero if one is, so a local minimum cannot exist in this somewhat unphysical $L_i \to \infty$ limit for a continuum transition.

III. MOLECULAR TARGET

The molecular case studied here applies to a randomly oriented one-electron diatomic with no vibronic degrees of freedom. This is a common model and the manner in which it relates to more realistic approximations to molecular inelastic scattering problems is discussed in a number of places.[28–30] This system is one of the few for which the electronic structure is well known and at the same time accurately models a target for which measure-

FIG. 1. Zeros for the $l = 0$, $\alpha = 1$ and $l = 1$, $\alpha = 1$ components, defined by Eq. (4), for the $3p \to 4d$ transition are shown by the solid and dashed lines, respectively. The two points at which the GOS is zero are indicated by the open squares. The magnitude of momentum transfer is $\hbar K$ and K is in units of a_o^{-1}.

ments can be made.

The Born matrix element for this model is usually[15,16,29] written as

$$\varepsilon(K,\delta,R) = \int d\mathbf{r}\, \psi_f^*(\mathbf{r};R) e^{i\mathbf{K}\cdot\mathbf{r}} \psi_i(\mathbf{r};R) , \qquad (7)$$

where the internuclear axis is taken to be collinear with the z axis and δ is the angle between $\mathbf{K}$ and $\mathbf{R}$. See Fig. 1 of Ref. 29. The initial and final electronic state's quantum numbers are indicated by i and f with $i \neq f$. Equation (7) can be reduced to a sum of one-dimensional integrals that parametrically depend upon δ for the exact Born-Oppenheimer wave functions $\psi(\mathbf{r};R)$.[29] This technique does minimize the numerical difficulty, but the result is awkward in the context of the present problem. An alternative method is now outlined that is more general and illuminating. It requires the evaluation of a series of two-dimensional integrals, but avoids considerable manipulation of the parameters in the problem.[29] Contemporary computers can efficiently calculate the two-dimensional integrals.

The azimuthal symmetry of the wave functions appearing in Eq. (7) can be utilized by writing the wave function in the form

$$\psi_i(\mathbf{r};R) = \Gamma_i(\lambda,\mu;R)[\exp(iM_i\phi)/\sqrt{2\pi}] ,$$

where the prolate spheroidal coordinates $1 \leq \lambda < \infty$, $-1 \leq \mu \leq 1$, and $0 \leq \phi \leq 2\pi$ are indicated since the one-electron diatomic molecule electronic Schrödinger equation separates in these coordinates. The integral over ϕ in Eq. (7) can be carried out with the result

$$\varepsilon(K,\delta,R) = (R/2)^3 \int d\lambda\, d\mu(\lambda^2-\mu^2)\Gamma_f(\lambda,\mu;R)$$

$$\times e^{iZ\cos\delta} J_\alpha(Y\sin\delta)\Gamma_i(\lambda,\mu;R) ,$$

$$\alpha \equiv |M_f - M_i| , \qquad (8)$$

$$Z \equiv (KR/2)\lambda\mu ,$$

$$Y \equiv (KR/2)[(\lambda^2-1)(1-\mu^2)]^{1/2} ,$$

and J_α is a Bessel function of the first kind. The right-hand side of Eq. (8) is multiplied by $(-1)^{M_i-M_f}$ if $M_i > M_f$. The Legendre functions P_n^α form a basis for $\varepsilon(K,\delta,R)$ and symmetry arguments[29] limit this expansion to the form

$$\varepsilon(K,\delta,R) = \sum_{l=0}^{\infty} \left[\frac{2i^l l!(l+\alpha+\frac{1}{2})}{(l+2\alpha)!} \right] \varepsilon_l^\alpha(K,R) P_{l+\alpha}^\alpha(\cos\delta) ,$$

$$(9)$$

and symmetry requires some $\varepsilon_l^\alpha(K,R)$ to be zero in the homopolar case. The expansion coefficients ε_l^α can be evaluated using the methods given in Ref. 29 to produce

$$\varepsilon_l^\alpha(K,R) = (R/2)^3 \int d\lambda\, d\mu(\lambda^2-\mu^2)\Gamma_f(\lambda,\mu;R)$$

$$\times P_{l+\alpha}^\alpha(\cos\Theta) j_{l+\alpha}(z)\Gamma_i(\lambda,\mu;R) ,$$

where

$$\cos\Theta \equiv \lambda\mu/[(\lambda^2+\mu^2-1)]^{1/2} , \qquad (10)$$

$$z \equiv (KR/2)[(\lambda^2+\mu^2-1)]^{1/2} ,$$

and j_n is a spherical Bessel of the first kind.

Equation (10) is more general than the derivation suggests. The same steps can be performed in any coordinate system with azimuthal symmetry. Different coordinate systems only require the replacement of z, Z, Y, $\cos\Theta$, and the volume element appearing in Eqs. (8) and (10) by the appropriate quantities. For example, it includes the single center expansion where additional integrals can be evaluated in terms of simple functions.[16]

The GOS is defined for the molecule case by replacing Eq. (3) with

$$|\varepsilon(K,R)|^2/K^2$$

$$\equiv (1/4\pi K^2) \int d\Omega(\hat{\mathbf{n}})|\varepsilon(K,\delta,R)|^2$$

$$= K^{-2} \sum_l \left[\frac{2(l)!(l+\alpha+\frac{1}{2})}{(l+2\alpha)!} \right] |\varepsilon_l^\alpha(K,R)|^2 , \qquad (11)$$

where the volume element $d\Omega(\hat{\mathbf{n}})$ is for a vector $\hat{\mathbf{n}}$ parallel to $\mathbf{R}$ in some space fixed axis.[16,29] As argued for the atomic case, Eq. (11) requires every $\varepsilon_l^\alpha(K,R)$ in Eq. (11) to equal zero for any R and K for which the GOS vanishes. Unlike the atom case, the range for l in Eq. (11) is independent of the initial and final states for the target and spans $[0,\infty)$. The atomic case to date indicates that requiring two such matrix elements to vanish is not common and no examples of finding three simultaneously equal to zero have been reported. Hence it seems unlikely that a molecular GOS can have a local zero for $0 < K < \infty$ and $0 < R < \infty$.

The likelihood of a local zero seems remote and suggests that a proof of impossibility could be achieved using the atomic case techniques. As pointed out in Sec. I, this same speculation was stated in Ref. 14. Such a proof was not found. The proof was also attempted by expanding the plane wave of Eq. (7) in prolate spheroidal coordinates[31] to take advantage of the separability of the one-electron diatomic molecule wave functions in these coordinates. This does reduce the problem to a relationship between one-dimensional matrix elements. The lack of recursion relationships for the spheroidal wave functions[31] prevents the establishment of linear dependency between these matrix elements if a local zero in the GOS occurs. Hence a proof that a local zero cannot occur is yet to be established.

The existence of striking structure in both the experimental[18,19] and theoretical[15,16] molecular GOS is a fact. The postulate made here that this structure is due to the vanishing of just one of the $\varepsilon_l^\alpha(K,R)$ is tested for the $1s\sigma_g \rightarrow 3p\sigma_u$ transition in H_2^+. Data for the total GOS and this transition are given in Ref. 15 and for the integrand of Eq. (11) in Ref. 16. Figure 2 shows $|\varepsilon(K,R)|^2/K^2$ for this transition in a region of K and R near a minimum. The GOS does not have a zero here. Further, values for $|\varepsilon_l^\alpha(K,R)|$ with $l=1,3,5$ and $\alpha=0$ are displayed. [Symmetry for this transition restricts Eq. (9) to $\alpha=0$ and odd l.] It is clear that $\varepsilon_l^\alpha(K,R)$ vanishes for $l=1$ and $\alpha=0$ at the minimum in the GOS while the $l=3,5$ terms remain finite.
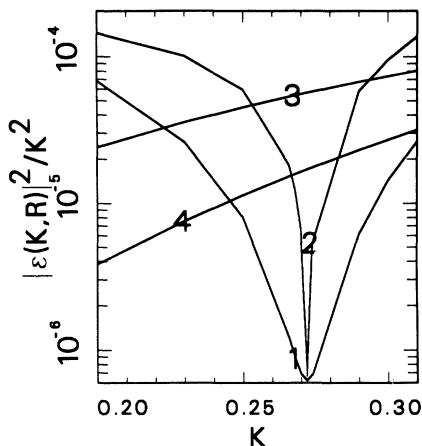
FIG. 2. Curve 1 is $|\varepsilon(K,R)|^2/K^2$ defined by Eq. (11) for the $1s\sigma_g \rightarrow 3p\sigma_u$ transition in H_2^+ for $R = 2.5a_o$ shown as a function of K. Curves 2, 3, and 4 are scaled values of $|\varepsilon_l^a(K,R)|$ from Eq. (9) for $l = 1,3,5$ with $\alpha = 0$. Curve 2 is $0.15|\varepsilon_1^0(K,R)|$, curve 3 is $0.70|\varepsilon_3^0(K,R)|$, and curve 4 is $110.0|\varepsilon_1^0(K,R)|$. K is in units of a_o^{-1}.

FIG. 4. Values of $|\varepsilon(K,R)|^2/K^2$ for the $1s\sigma_g \rightarrow 2s\sigma_g$ transition in H_2^+ are shown as a function of R and K. R is units of a_o and K is in units of a_o^{-1}.

The DOS for the sequence of transitions $1s\sigma_g \rightarrow np\sigma_u$, $n \geq 3$ has an isolated zero near $R = 2a_0$.[24,25] Figure 3 shows Eq. (11) for the $1s\sigma_g \rightarrow 4p\sigma_u$ transition. As anticipated, the structure shown in Ref. 7 and that shown here for the next member of this sequence are very much alike. The DOS isolated zero is clearly connected to the minimum in the GOS as a function of K and R and, as shown in Fig. 2, this minimum occurs when $\varepsilon_1^0(K,R) = 0$.

Figure 4 shows $|\varepsilon(K,R)|^2/K^2$ of Eq. (11) for the $1s\sigma_g \rightarrow 2s\sigma_g$ transition. The DOS and all $\varepsilon_l^0(K,R)$ for l odd are zero for all R and none of the unusual structure
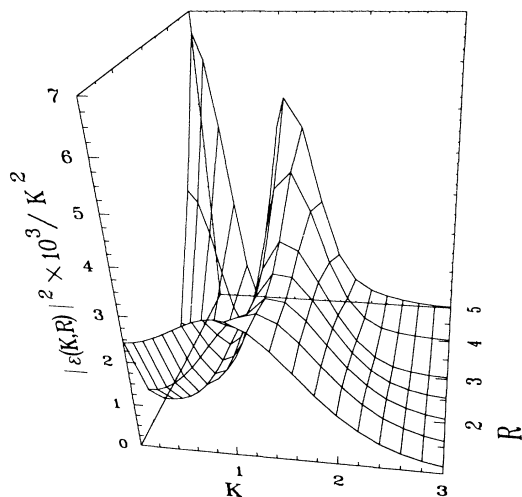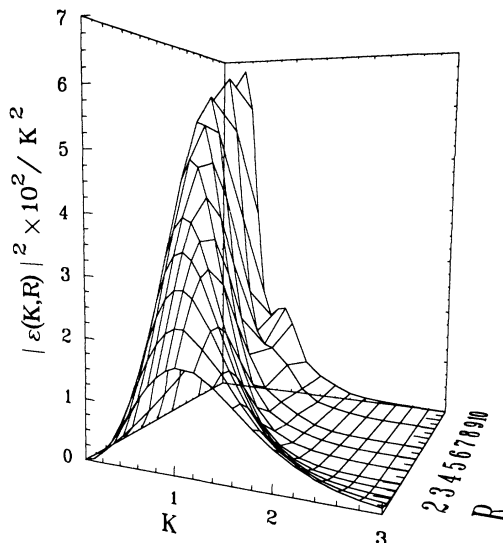

FIG. 3. Values of $|\varepsilon(K,R)|^2/K^2$ for the $1s\sigma_g \rightarrow 4p\sigma_u$ transition in H_2^+ are shown as a function of internuclear separation R and of K. R is in units of a_o and K is in units of a_o^{-1}.

associated with an isolated zero in the DOS, as shown in Fig. 3, occurs for this case. The nonvanishing terms in Eq. (9) are $\varepsilon_l^0(K,R)$ for even l. One of these matrix elements could vanish for $K > 0$ and introduce structure into the GOS, but does not in this case. Evidence for a weak minimum occurring at $KR \simeq 7$ is evident. This structure is due to the interference associated with the rotation of the internuclear axis.[22]

The question arises about the behavior associated with the occurrence[25] of a transition with a zero DOS at $R = 0$, but nonzero for $R > 0$. Examples of this are the $1s\sigma_g \rightarrow 6h\sigma_u$ and $1s\sigma_g \rightarrow 4f\sigma_u$ transitions, which are shown in Figs. 5 and 6. The zero in $\varepsilon_1^0(K,R)$ as K and R approach zero correlates to an atomic matrix element that must vanish due to angular momentum effects rather than in radial integral considerations. This information is contained in $\varepsilon_1^0(K,R)$, but the character of its behavior in the atom limit is yet to be made transparent. However, structure qualitatively like that shown for the $1s\sigma_g \rightarrow np\sigma_u$, $n \geq 3$ sequence is evident. The $1s\sigma_g \rightarrow 6h\sigma_u$ transition, Fig. 5, has a small DOS relative to the GOS for $K > 0$ and the minimum is not a striking feature, while the reverse is true for the $1s\sigma_g \rightarrow 4f\sigma_u$ transition, Fig. 6. The Fig. 5 behavior is somewhat like the experimental data[19] for a transition in CO.

As one last demonstration, Fig. 7 shows the GOS for the $2s\sigma_g \rightarrow 5f\sigma_u$ transition. This DOS has isolated zeros for $R = 0$ and $R \simeq 5.5a_0$.[24,25] The minimum associated with the DOS zero at $R = 0$ is not clearly evident in Fig. 7 and, like the case shown in Fig. 5, is due to the small $\varepsilon_1^0(K,R)$ relative to $\varepsilon_3^0(K,R)$. The interesting ridge in the $R \leq 7a_0$, $K \simeq 0.7a_0^{-1}$ region is mainly due to $\varepsilon_3^0(K,R)$. This matrix element has a pair of zeros occurring at small and large K for small R. As R increases, these two zeros approach each other and finally converge to a second-
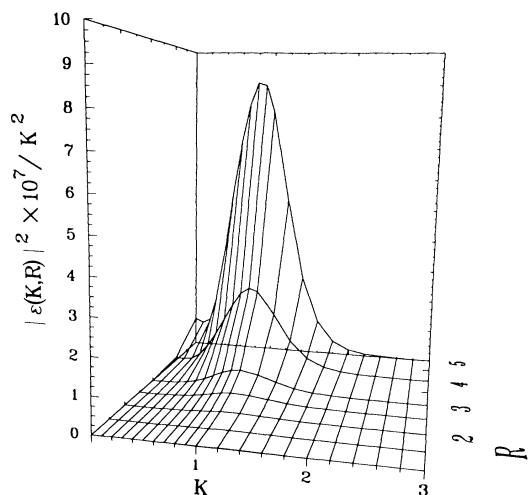
FIG. 5. Values of $|\varepsilon(K,R)|^2/K^2$ for the $1s\sigma_g \to 6h\sigma_u$ transition in H_2^+ are shown as a function of R and K. R is in units of a_o and K is in units of a_o^{-1}.

order zero near the large-R terminus of this ridge $R \simeq 8a_0$. This pair of zeros vanish from the real plane for larger R. All of the coefficients considered in the Eq. (9) expansion for this case display similar character. The structure associated with the zero in $\varepsilon_1^0(K,R)$ for $R \geq 5.5a_0$ and $K \simeq 0.2a_0^{-1}$ is typical of that shown in the preceding examples.

The relationship between the zero in the DOS and the minimum in the GOS seems clearly established for the H_2^+ transitions considered here. These minima do not appear to be zeros but are associated with a zero in $\varepsilon_1^\alpha(K,R)$. Other matrix elements appearing in Eq. (11)
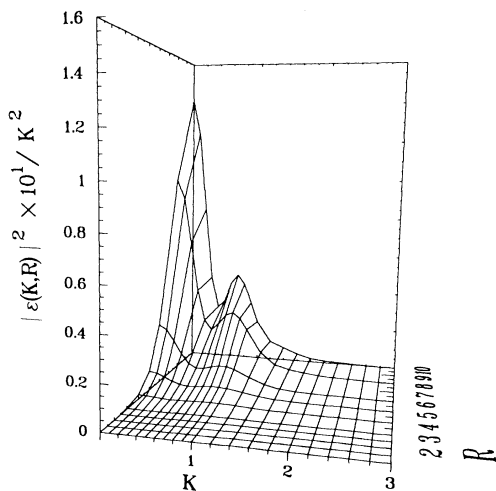
can cause structure in the GOS and one case, the $2s\sigma_g \to 5f\sigma_u$ transition, responding to $\varepsilon_l^\alpha(K,R)=0$ for both $l = 1, 3$ was found.

The central role of zeros in the DOS for the molecular case brings attention to the nature of these zeros. Much is known about the atomic case, but one example is now discussed to point out the rather striking differences displayed by molecules. The one-electron homopolar diatomic molecule is known to have single zeros for $0 < R < \infty$ in the $1s\sigma_g \to np\sigma_u$, $n \geq 3$ sequence, hence the matrix elements in the atomic DOS must have different signs for the atomic states to which the molecule correlates for $R=0$ and $R \to \infty$. These are the usual hydrogenic matrix elements for $R =0$ and $R \to \infty$ which have recently been shown to have[23] the same sign. If they have the same sign for the limiting values of R they cannot have an odd number of zeros for the intermediate R values.

The fallacy in the above argument is in the implicit assumption that the phase of the wave functions does not change as a function of R. The $3p\sigma_u$ state for the homopolar diatomic molecule is an example of this change in phase at some intermediate R. This state is constructed for $R \to \infty$ of an appropriate mixture of an antisymmetric combination of the $2s$ orbitals on each nucleus and a symmetric combination of $2p_0$ orbitals on each nucleus if the $2p_0$ orbitals are aligned with their positive lobes in the same direction.[32] As $R \to 0$ this state is more accurately represented by a single $3p_0$ orbital located at the midpoint of R. However, to preserve the sign of the wave function in the region of the nodal plane perpendicular to the internuclear line and at its midpoint the $3p_0$ orbital must be rotated $180°$ with respect to the orientation chosen for the $2p_0$ orbitals in the large-R region. Hence,
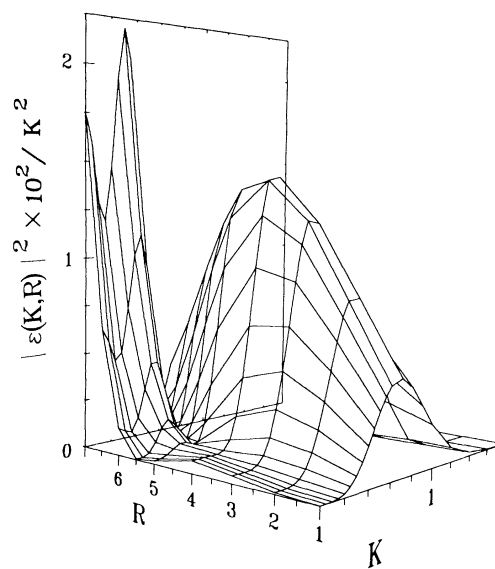

FIG. 6. Values of $|\varepsilon(K,R)|^2/K^2$ for the $1s\sigma_g \to 4f\sigma_u$ transition in H_2^+ are shown as a function of R and K. R is in units of a_o and K is in units of a_o^{-1}.

FIG. 7. Values of $|\varepsilon(K,R)|^2/K^2$ for the $2s\sigma_g \to 5f\sigma_u$ transition in H_2^+ are shown as a function of R and K. R is in units of a_o and k is in units of a_o^{-1}.

in calculating the DOS matrix elements for $R = 0$ and $R \to \infty$ the $1s$-$3p_0$ and $1s$-$2p_0$ (the $1s$-$2s$ components necessarily vanish) matrix elements reflect this change in sign convention by having different signs. This, then, allows an odd number of zeros to appear in the DOS for the $1s\sigma_g \to 3p\sigma_u$ transition.

The molecule case is also quite different from the atom case in that the atom DOS appears not to have zeros for transitions involving one state that is nodeless.[4] The $1s\sigma_g$ state is nodeless, so isolated zeros in the $1s\sigma_g \to np\sigma_u$, $n > 2$ sequence do not have atomic analogs. This difference is clearly due to the phase change, noted in the above paragraph, that is unique to molecules.

IV. SUMMARY

The existence of an isolated zero in the atom generalized oscillator strength was shown to depend on $\min(L_f, L_i)$. Many examples of zeros are known when $\min(L_f, L_i) = 0$ and one example was given here for $\min(L_f, L_i) = 1$. A number of examples of nonzero minima are known to occur due to the vanishing of just one of the matrix elements in the GOS expression.[6] It was shown that the atomic GOS cannot have an isolated zero in the somewhat unphysical limit of both L_i and L_f approaching infinity in a certain manner.

Equations were derived for the one-electron diatomic molecule case and, using the atomic results as a guide, the possibility of an isolated zero appears unlikely. However, a proof that one cannot exist was not established here. Theoretical results for H_2^+ show minima[15,16] as does H_2O.[14] The equations for H_2^+ were investigated and the minima were shown to correspond to a zero in a matrix element related to the dipole oscillator strength while other nonzero matrix elements in the GOS expression keep these minima from attaining a zero value. The known theoretical minima for H_2^+ were shown to correlate, as a function of internuclear separation as the momentum-transfer magnitude approached zero, to a

zero in the dipole oscillator strength. Additional numerical examples were considered and the existence of a zero in the dipole oscillator strength[25] always predicts the existence of minima in the generalized oscillator strength for finite magnitude of the momentum transfer. Unusual structure due to pairs of zeros in a higher term of the expansion derived here was shown for the $2s\sigma_g \to 5f\sigma_u$ transition.

A required change in phase convention as a function of internuclear distance was noted for the $np\sigma_u$, $n > 2$ homopolar one-electron diatomic molecule wave functions. This is responsible for the existence of isolated zeros[25] in the $1s\sigma_g \to np\sigma_u$ dipole oscillator strengths, the structure found in their generalized oscillator strengths,[15,16] and the qualitative differences between the properties of atom and molecule dipole oscillator strengths discussed in Sec. III.

Experimental data show characteristics qualitatively like some of the examples given here. The CO case[19] has a shallow minimum and appears more like the $1s\sigma_g \to 6h\sigma_u$ transition than those with dominant dipole transitions. The existence of an experimental local minimum consistent with a zero in a generalized oscillator strength for H_2O (Ref. 18) motivates the need for additional information. A rigorous proof of the speculations made here about their improbable existence, if possible, would be useful because of the difficulty of establishing a zero by experimental techniques. The relationship between the GOS and DOS structure claimed here implies a zero in the H_2O DOS for this transition for some internuclear configuration, perhaps not too far from the equilibrium internuclear configuration, exists. Experimental or theoretical evidence concerning this possibility would be of interest.

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