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Additional information on J. Chem. Phys.

molecular parameters are shown in Table III along with the effect of the variation made for μ_0 and α_e.

It seems to be clear that a successful molecular theory for dielectric behavior of polar gases must include careful considerations of the large effect of molecular shape.

[1] C. L. Kong, J. Chem. Phys. **53**, 1516 (1970).
[2] C. L. Kong, J. Chem. Phys. **53**, 1522 (1970).
[3] M. D. McKinley and T. M. Reed III, J. Chem. Phys. **42**, 3891 (1965).
[4] H. Sutter and R. H. Cole, J. Chem. Phys. **52**, 132 (1970).
[5] See the results of Sutter and Cole as well as the various references cited in Ref. 4.

Many-Body Approach to the Jahn–Teller Problem

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We discuss the application of Green's function techniques to a simple Hamiltonian which has been studied by more conventional quantum mechanical techniques. The Hamiltonian is that for two degenerate electronic states interacting through a two fold degenerate vibrational mode—a Jahn-Teller problem.[1] We hope that this simple, but nontrivial problem can be used as a laboratory for the application of Green's function techniques to molecular and solid state vibronic problems. This Hamiltonian has been diagonalized exactly[1] and some simple approximation schemes have been proposed[2]; therefore, comparison of the present techniques with the exact results is possible.

The Hamiltonian may be written

$$\mathcal{K} = \epsilon(c_\alpha^+ c_\alpha + c_\beta^+ c_\beta) + \omega(b_l^+ b_l + b_{-l}^+ b_{-l})$$
$$+ \gamma\omega\{c_\alpha^+ c_\beta(b_{-l}^+ + b_{+l}) + c_\beta^+ c_\alpha(b_{-l} + b_{+l}^+)\}, \quad (1)$$

where c_α^+ and c_β^+ create electronic excitations of symmetry type α and β, respectively, and b_l^+ and b_{-l}^+ create phonons of symmetry type l and $-l$. (There is a constant of motion in this problem which is a quasi-angular momentum.)[1] If we define the Green's function, $G_\alpha(z)$ as[3] $\langle c_\alpha(z-\mathcal{K})^{-1}c_\alpha^+ \rangle$, where the average is over the ground state of the system (the state with no phonons or excitations), then it is easy to see that the poles of $G_\alpha(z)$ are the eigenvalues of $\mathcal{K}$. We discuss two procedures for finding these poles: an approximate calculation of the self-energy of $G_\alpha(z)$ using the functional derivative technique,[4] and an exact diagrammatic expansion of $G_\alpha(z)$. The self-energy, $\Sigma_\alpha(z)$, is defined by $G_\alpha^{-1}(z) = z - \epsilon - \Sigma_\alpha(z)$.

In the functional derivative technique, a more general Green's function is defined with a fictitious external potential.[3] When this potential is removed, the original problem is regained. Using this technique, one finds the equation for the second-order approximation to the self-energy to be:

$$\Sigma_\alpha^{(2)}(z) = \gamma^2 \omega^2 G_\alpha(z-\omega). \quad (2)$$

This equation is the simplest prototype of those found using similar techniques for the treatment of electron–phonon interactions in solids.[5] Equation (2) is an equation for the self-energy which has many solutions; in particular, defining $\Sigma_\alpha^{(2)}(z)$ for $z=0$ to $z=\omega$ defines $\Sigma_\alpha^{(2)}(z)$ for all z via Eq. (2). However, we have found a solution of Eq. (2) which satisfies the correct boundary conditions and is continuous in z along the real axis except for simple poles. We find[6]

$$\Sigma_\alpha^{(2)}(z) = -\gamma\omega[J_{\nu+1}(2\gamma)/J_\nu(2\gamma)], \quad (3)$$

where J_n is the usual Bessel function and $\omega\nu = \epsilon - z$. The continued fraction form of $\Sigma_\alpha^{(2)}(z)$ is given in Ref. 6 and can be found by iteration of Eq. 2. It turns out that the poles of $G_\alpha(z)$ are the zeros of $J_{\nu-1}(2\gamma)$. Notice that the energy, z, appears in the *order* of the Bessel function.

In the diagrammatic analysis, one writes down the irreducible diagrams representing $\Sigma_\alpha(z)$ and finds that $\Sigma_\alpha(z)$ can be written as another Green's function:

$$\Sigma_\alpha(z) = \gamma^2 \omega^2 G_\alpha'(z) \equiv \gamma^2 \omega^2 \langle c_\beta b_l(z-\tilde{H})^{-1} b_l^+ c_\beta^+ \rangle, \quad (4)$$

where $\tilde{H} = H_0 + \gamma PVP$, and P is the projection operator out of the state $c_\alpha^+ |0\rangle$. There is a simple correspondence between (4) (and its further consequences) and Mori's Brownian motion theory[7]: $G_\alpha(z)$ corresponds to the zeroth-order response function, $\Sigma_\alpha(z)$ the first-order response, etc. Using (6) and finding the self-energy of $G_\alpha'(z)$ and so on, we find a continued fraction form for $\Sigma_\alpha(z)$ which differs from that for $\Sigma_\alpha^{(2)}(z)$ in the second term. We have found the poles of $G_\alpha(z)$ using this form of $\Sigma_\alpha(z)$ and find agreement with the results of Longuet-Higgins, *et al.*[1] On the other hand, the poles of $G_\alpha(z)$ calculated with $\Sigma_\alpha^{(2)}(z)$ are correct only for very small γ (in fact, for $\gamma \gtrsim 1$ the poles seem to be linear in γ). However, using $\Sigma_\alpha^{(2)}(z)$ does give an infinite number of poles, all of which approach the correct limit as $\gamma \rightarrow 0$.

In conclusion, we may say that although the equations for $\Sigma_\alpha(z)$ and $\Sigma_\alpha^{(2)}(z)$ are similar, the results for

the eigenvalues are very different, and one must use the second-order approximation in the functional derivative method with care. Of course, in a true many-body system, there may tend to be cancellations which will bring the approximation closer to the exact answer. However, the fact that the energy dependence of the self-energy occurs in *the order of a Bessel function* seems to imply that solutions to similar equations in the electron–phonon case will have exceedingly complicated energy dependences.

Two more comments are in order. The first is that the form of $\Sigma_\alpha^{(2)}(z)$ is the same as that which would arise using the functional derivative technique in the simpler problem of a single electronic state system with linear coupling to one vibrational mode. Hence, to second order, the functional derivative technique cannot distinguish the Jahn–Teller problem from the displaced oscillator. Secondly, if we go to the next most complicated problem, the pseudo Jahn-Teller case, where the electronic degeneracy is split, the diagrammatic analysis no longer yields a simple expression such as (6) for $\Sigma_\alpha(z)$. This is due to the introduc-

tion of "crossing" diagrams admitted when the quasi angular momentum is no longer a constant of motion. This is also a feature of the more general electron-phonon problems.

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[1] H. C. Longuet-Higgins, U. Öpik, M. H. L. Pryce, and R. A. Sack, Proc. Roy. Soc. (London) **A244**, 1 (1968). W. Moffit and W. Thorson in *Calcul des Fonctions d'onde Moléculaire* (Recherche Memoire Centre National de la Recherche Scientifique, Paris, 1958).

[2] B. Halperin and R. Englman, Solid State Commun. **7**, 1579 (1969). W. D. Hobey, J. Chem. Phys. **43**, 2187 (1965). D. E. McCumber, J. Math. Phys. **5**, 508 (1964). J. S. Alper and R. Silbey, J. Chem. Phys. **51**, 3129 (1969).

[3] D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [Sov. Phys. Usp. **3**, 320 (1960)].

[4] L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (Benjamin, New York, 1965).

[5] See, e.g., R. D. Puff and G. Whitfield in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Plenum, New York, 1962).

[6] G. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge U. P., London, 1922).

[7] H. Mori, Progr. Theoret. Phys. (Kyoto) **34**, 399 (1965).

On the Internal Conversion in Fluorescein Dyes

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In previous papers[1,2] evidence was presented for the occurrence of an efficient internal conversion process in a xanthene dye, 6-hydroxy-9-phenylfluorone (HPF), by comparison of the fluorescence and triplet yields for this compound with those for fluorescein (Fl). In the
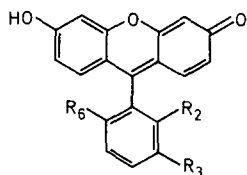
	HPF	Fl	3-CFl	6-CFl
R_2	H	COOH	COOH	COOH
R_3	H	H	COOH	H
R_6	H	H	H	COOH

solvent used—$0.01M$ NaOH in water—these dyes are present in their monoanionic and dianionic forms, respectively. Their absorption spectra in the visible are under these conditions almost identical; however, whereas the fluorescence yield of Fl is close to unity (0.92)[3] that of HPF is only 0.21.[1] The triplet yield of HPF is lower than that of Fl in the same proportion. The carboxylate group thus is responsible for the absence of internal conversion in Fl; its action was tentatively attributed to the hydration of the carboxylate group, which creates an ordered solvent structure in the vicinity of the xanthene group and thus

increases the rigidity of this group. This hypothesis was based upon the observation that the fluorescence and triplet yields of fluorescein are decreased to those of HPF in acid solution where the carboxylate group is protonated and the hydration reduced.

Recently, Fink and Willis[4] reported a study of the fluorescent properties of 6-hydroxy-9-(3-carboxy)phenylfluorone(HCPF). They found that the fluorescence yield of this compound, in alkaline as well as acid solution, is very close to that of HPF, and they concluded that the solvation effect is not governing the fluorescence yield. Instead, an alternative explanation was put forward, based upon the assumption of the occurrence of Fl in its lactonic form in alkaline solution. However, the spectral properties of Fl and HPF are almost identical and this assumption therefore cannot be valid. It is known that the lactonic form of neutral Fl does not absorb in the visible,[5] and the corresponding divalent anion would not be expected to absorb in this spectral range either. On the other hand, their results do not invalidate our hypothesis since the carboxyl group in HCPF may not be close enough to the xanthene part of the dye to interact by a solvation effect.

We wish to report results of a study of 3'-carboxyfluorescein (3-CFl) which provides further arguments