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COMMENTS

COMMENT ON "Green's functions in the theories of radiationless transitions, complex molecular spectra and resonant Raman cross sections"

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Problems related to the time evolution and scattering characteristics of systems containing complex level-schemes (i.e., coupled discrete states and continua) are common to many branches of Physics, e.g., high-energy and nuclear physics [1–3], solid state [4], atomic and molecular physics [5–7]. Extremely powerful methods for the theoretical treatment of such problems were suggested by Feschbach [1] in nuclear physics. These methods were later extended [3] and applied [5,6] to various systems.

In a recent paper [8] Hong suggested a new method for the handling of the problem of n coupled discrete states interacting with radiative and non-radiative continua. It is the purpose of the present note to demonstrate that the powerful methods mentioned above provide a simpler way for handling this problem and even more complicated problems. Let us first briefly recall some of the basic results of Feschbach's projection operator technique [1].

(1) Suppose we have a zero-order hamiltonian (H_0) whose spectrum consists of n discrete states as well as a number of continua (of any sort). These discrete states and continua may be coupled by an arbitrarily complex coupling operator V.

(2) The total Hilbert space defined in (1) may be divided into two (or more) subspaces. For example, one can define a $\hat{P}$ space containing the n discrete states and a complementary $\hat{Q}$ space.

(3) The time evolution and scattering properties of the $\hat{P}$ space are described by the $n \times n$ $\hat{P}G\hat{P}$ matrix [2] which may be obtained by the inversion of the $n \times n$ $E - H_{\text{eff}}$ matrix, i.e.,

$$\hat{P}G\hat{P} = (E - \hat{P}H_{\text{eff}}\hat{P})^{-1}\hat{P}\,, \tag{1}$$

H_{eff} being the effective hamiltonian defined as

$$H_{\text{eff}} = H_0 + V + V\hat{Q}\tilde{G}\hat{Q}V\,, \tag{2}$$

and

$$\tilde{G} = (E - H_0 - \hat{Q}V\hat{Q})^{-1}\hat{Q}\,. \tag{3}$$

(4) Other projections of the molecular Green function ($\hat{P}G\hat{Q}$, $\hat{Q}G\hat{P}$, $\hat{Q}G\hat{Q}$) may be obtained using $\hat{P}G\hat{P}$ after some manipulations [3]

$$\hat{P}G\hat{Q} = \hat{P}G\hat{P}V\hat{Q}\tilde{G}\hat{Q}\,, \tag{4}$$

$$\hat{Q}G\hat{P} = \hat{Q}\tilde{G}\hat{Q}V\hat{P}G\hat{P}\,, \tag{5}$$

$$\hat{Q}G\hat{Q} = \tilde{G} + \tilde{G}\hat{Q}V\hat{P}G\hat{P}V\hat{Q}\tilde{G}\,. \tag{6}$$

This formalism, apart from reducing the dimensionality of the problems at hand enables us to carry out partial summations, treat problems to different order in various interaction terms and have an insight into the formal properties of the solutions.

In Hong's treatment of the problem [8] he assumes (i) that the secondary states (belonging to $\hat{Q}$) are not coupled among themselves (eq. (1) of ref. [8]). However, Hong allows the zero-order Green function (G_0) to be non-diagonal in the zero-order basis set. His solution requires the inversion of a $2n \times 2n$ matrix. The following remarks should now be made:

(a) The same problem without assumption (i) but when G_0 is diagonal has a general solution by inverting the $n \times n$ matrix [1–3] [eqs. (1) and (2)].

(b) G_0 may always be *chosen* to be diagonal [as assumption (i) is relaxed].

(c) A number of complex problems involving interacting continua have been treated using projection operators in terms of $n \times n$ matrices [6,9–11].

In summary, existing powerful projection operator techniques can provide solutions to even more complex systems than those treated by Hong.

References

[1] H. Feschbach, Ann. Rev. Nucl. Phys. 8 (1958) 49.
[2] M.L. Goldberger and R.M. Watson, Collision Theory (Wiley, New York, 1964).
[3] L. Mower, Phys. Rev. 142 (1966) 799.
[4] A.A. Maradudin, Solid State Phys. 18 (1966) 273.
[5] C. Cohen Tannoudji, Complement de Mechanique Quantique, Cours de 3e Cycle (Polycopie, Paris, 1966).
[6] J. Jortner and S. Mukamel, in: The World of Quantum Chemistry, eds. R. Daudel and P. Pullman (Reidel, Dordrecht, Holland, 1974).
[7] G.W. Robinson, in: Excited States, Vol. 1, ed. E.C. Lim (Acad. Press, New York, 1974).
[8] H.K. Hong, Chem. Phys. 9 (1975) 1.
[9] J. Jortner and S. Mukamel, in: MTP International Review of Science, Series 2, Vol. 1 (Theoretical Chemistry) ed. A.D. Buckingham (Butterworths, 1975) p. 327.
[10] S. Mukamel and J. Jortner, Mol. Phys. 27 (1974) 1543; J. Chem. Phys. 60 (1974) 4760; 61 (1974) 227.
[11] S. Mukamel, A. Ben-Reuven and J. Jortner, Phys. Rev. A12 (1975) 947.