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# Aspects of Time-Dependent Perturbation Theory*

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The Dirac variation-of-constants method has long provided a basis for perturbative solution of the time-dependent Schrödinger equation. In spite of its widespread utilization, certain aspects of the method have been discussed only superficially and remain somewhat obscure. The present review attempts to clarify some of these points, particularly those related to *secular* and *normalization* terms. Secular terms arise from an over-all time-dependent phase in the wave function, while normalization terms preserve the norm of the wave function. A proper treatment of the secular terms is essential in the presence of a physically significant level shift that can produce *secular divergences* in the time-dependent perturbation functions. The normalization terms are always important, although the formulation of a simple method for including them is of greatest utility in applications requiring higher-order perturbation theory (e.g., nonlinear optical phenomena), where difficulties have arisen in previous treatments. Although the Dirac perturbation technique includes the correct secular and normalization terms when properly executed, it is convenient to reinterpret the perturbation problem so that the secular and normalization terms can be factored from the wave function to all orders. It is shown that an appropriate over-all multiplicative, time-dependent normalization and phase factor can be obtained, and that it is simply the amplitude for finding the system in the unperturbed eigenstate at any time $t$. The regular part of the wave function remaining after this factorization provides a complete description of the physical properties of the system of interest and determines the over-all normalization and phase, as well. Most important, the regular function and its perturbation expansion satisfy equations which are more convenient for computational applications than are the customary Dirac equations, and, in contrast to the latter, they reduce directly to the familiar *time-independent* perturbation equations in the static limit. To illustrate the general development, the model problem of a linearly perturbed harmonic oscillator and the static, harmonic, and electromagnetic perturbations of arbitrary quantum-mechanical systems are treated explicitly. In the case of an adiabatically applied static perturbation, the familiar adiabatic theorem is recovered with the over-all phase factor giving the perturbed eigenvalue, while in the case of an harmonic perturbation, the over-all phase factor obtained includes the system level shift appropriate for a quasiperiodic state. For an electromagnetic perturbation, compact expressions are obtained for various nonlinear optical susceptibilities in forms suitable for computations. Time-dependent Hartree–Fock approximations are treated explicitly to demonstrate that difficulties can arise when normalization and secular terms are not extracted prior to application of the perturbation formalism. Connection is also made with other methods which can be employed to eliminate secular and normalization terms from the wave function; these include a projection procedure and multiple-time-scales perturbation theory. The elimination of secular divergences from the perturbation functions is shown to be important for the construction of a valid Fourier transform. Secular and normalization terms also arise in connection with variational principles for the time-dependent Schrödinger equation. By employing the Frenkel variational principle and an ansatz for the total wave function that explicitly isolates the secular and normalization terms, a computationally convenient variational functional is obtained. This form of the Frenkel principle provides a bound to the system level shift induced by an oscillatory perturbation and is equivalent to the Ritz variational principle in the static limit. Explicit expressions for the variational functional in the Hartree–Fock approximations are derived in forms suitable for computational applications to the interactions of radiation and matter.

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## I. INTRODUCTION

The variation-of-constants method introduced by Dirac[1] has long served as the basis for perturbative

[1] Introduction of the variation-of-constants method for the quantum treatment of the interaction of radiation and matter is generally attributed to Dirac (1926, 1927a, b). See also the early papers of Born (1926), Schrödinger (1926a, b), and Slatre (1927).

solution of the time-dependent Schrödinger equation.[2] His technique is ideally suited for the treatment of many phenomena which require only the first- or second-order interaction between a finite number of states of the system of interest and an external perturbation,[3,4] and is particularly useful for the clarification of resonance or transition phenomena. However, considerable attention has been focused recently on the higher-order dispersive and absorptive processes connected with nonlinear optical phenomena,[5] which generally involve spectral sums over infinite numbers of virtual intermediate states when the Dirac approach is employed. The Dirac expansion in terms of multiple sums over a complete set of eigenstates, although correct in its essential features, becomes rather cumbersome for such higher-order interactions, and makes difficult the quantitative determination of the associated nonlinear optical susceptibilities.[6] To avoid the consequent summation difficulties, variation-perturbation methods have been formulated for the time-dependent quantum-mechanical perturbation problem.[7] These procedures have been shown to be useful in recent computational applications[8] and to provide concise expressions for nonlinear optical susceptibilities.[2]

In spite of the widespread utilization of the Dirac perturbation method and its variational analogs for the study of the semiclassical interaction of radiation and matter, certain aspects of the treatment have been discussed only superficially in the literature and apparently still remain somewhat obscure. Specifically, the identification of an over-all time-dependent phase in the wave function, its connection with physically observable level shifts, and the particular form in which such a phase factor appears in perturbative treatments are topics that require clarification. It is well-known that time-divergent terms arise in the perturbation solution of the Schrödinger equation for an adiabatically switched-on static perturbation, and that such "secular divergences" result from the perturbation expansion of an over-all phase in the wave function which contains the system energy level shift.[9] Similar level shifts and associated secular divergences also arise in the presence of time-dependent perturbations; they appear, for example, in second- and higher-order in the presence of an oscillatory radiation field,[10] and give rise to experimentally observable "light shifts."[11] However, while level shifts and their associated secular divergences are familiar in the static case, and the second-order level shift in a radiation field is well-known, a unified treatment of the more general secular terms which appear in

[2] An excellent review of the subject which cites many recent computational applications is given by Dalgarno (1966).

[3] We refer particularly to the semiclassical interaction of radiation and matter, described by Klein (1927) and Wentzel (1927). More recent discussions of the range of validity of the semiclassical approximation are given by Jaynes and Cummings (1963), Buckingham (1965), Crisp and Jaynes (1969), Stroud and Jaynes (1970), and Nesbet (1971a, b). See also Hameka (1965) and the recent article by Scully and Sargent (1972).

[4] Applications of the semiclassical approximation in molecular optics are given by Korff and Breit (1932), Breit (1932, 1933), Condon (1937), Condon, Altar, and Eyring (1937), Kauzman, Walter, and Eyring (1940), Moffitt and Moscowitz (1959), and Moscowitz (1962).

[5] Various aspects of nonlinear optical phenomena are reviewed by Franken and Ward (1963), Bloembergen (1965), Minck, Terhune, and Wang (1966), Pershan (1966), Kelley, Lax, and Tannenwald (1966), Buckingham and Orr (1967), Peticolas (1967), Suvoroy and Sonin (1967), and Rez (1968).

[6] Explicit expressions for many of the nonlinear optical susceptibilities have been tabulated by Ward (1965), who employs a diagrammatic technique to construct the multiple sums over virtual intermediate states. Extensions and corrections of this technique are given by Orr and Ward (1971). Although Ward's expressions are not directly suitable for computational applications, they do provide the explicit frequency dependence of the nonlinear susceptibilities and can be used in conjunction with closure approximations, such as that suggested by Dawes (1968). The accuracy of such closure techniques is somewhat difficult to assess, however. See, for example, the discussion of Klingbeil, Kaveeshwar, and Hurst (1972).

[7] Variational techniques for perturbative solution of the time-dependent Schrödinger equation have been devised recently by Karplus (1962), Mavroyannis and Stephen (1962), Karplus and Kolker (1963a), Yaris (1963, 1964), McLachlan (1964), Gurtin (1965), Rebane (1966), Chang (1966), Deal and Kestner (1966), Adamov, Orlov, and Rebane (1968), Epstein (1968a), Kestner, Young, and Deal (1968), Robinson (1969a, b), Broussard and Kestner (1970), and Chang (1971, 1972a, b). Moment-theory approaches, which are closely related to the variational techniques, can also be employed to circumvent the spectral sums of the Dirac expansions for the optical and related properties of atoms and molecules. See, for example, Langhoff and Karplus (1967, 1969, 1970a, b, c), Gordon (1968), Langhoff, Gordon, and Karplus (1971), Langhoff (1971a, b, c, 1972), Langhoff and Yates (1972), and references cited therein.

[8] Variational computations of linear and nonlinear optical and related properties of atoms and molecules are given by, for example, Karplus (1964), Chan and Dalgarno (1965), Kolker and Michels (1965), Victor, Browne, and Dalgarno (1967), Johnson, Epstein, and Meath (1967), Chung (1968), Grasso, Chung, and Hurst (1968), Sitz and Yaris (1968), and Kamikawai, Watanabe, and Amemiya (1969).

[9] The secular divergence problem is generally avoided in the static case by first introducing an appropriate ansatz for the wave function, $\Psi_s(\mathbf{r}, t) = (\chi_s^{(0)}(\mathbf{r}) + \chi_s^{(1)}(\mathbf{r}) + \cdots) \exp[(i\hbar)^{-1}(E_s^{(0)} + E_s^{(1)} + \cdots)t]$, and subsequently employing time-independent perturbation theory to determine the static perturbation functions, $\chi_s^{(n)}(\mathbf{r})$, and energies, $E_s^{(n)}$. See, for example, Hirschfelder, Byers-Brown, and Epstein (1964). The time-dependent perturbation functions, $\Psi_s(\mathbf{r}, t) = \Psi_s^{(0)}(\mathbf{r}, t) + \Psi_s^{(1)}(\mathbf{r}, t) + \cdots$, obtained from the Dirac approach incorporate the expansion of the exponential level shift factor. Consequently, the functions $\Psi_s^{(n)}(\mathbf{r}, t)$ contain time-diverging secular terms of the form, $\Psi_s^{(1)}(\mathbf{r}, t) = [\chi_s^{(1)}(\mathbf{r}) + (i\hbar)^{-1}\chi_s^{(0)}(\mathbf{r})E_s^{(1)}t] \exp[(i\hbar)^{-1}E_s^{(0)}t]$, $\Psi_s^{(2)}(\mathbf{r}, t) = [\chi_s^{(2)}(\mathbf{r}) + (i\hbar)^{-1}\chi_s^{(0)}(\mathbf{r})E_s^{(2)}t + (i\hbar)^{-1}\chi_s^{(1)}(\mathbf{r})E_s^{(1)}t + 1/2(i\hbar)^{-2}(E_s^{(1)}t)^2\chi_s^{(0)}(\mathbf{r})] \times \exp[(i\hbar)^{-1}E_s^{(0)}t]$, $\cdots$. Such secular divergences do not necessarily lead to formal difficulties, however, since they do not contribute to the expectation values of Hermitian operators and, moreover, their origin is perfectly clear. Furthermore, the secular divergent terms in the functions $\Psi_s^{(n)}(\mathbf{r}, t)$ are necessary to insure that the time-dependent perturbation equations reduce to the correct static counterparts for the $\chi_s^{(n)}(\mathbf{r})$ and $E_s^{(n)}$. Introductory discussions of secular terms are given by Bohm (1951) pp. 448–453, and Kramers (1957) pp. 209–223.

[10] General theoretical treatments of the level shift which arises in the presence of an oscillatory perturbation are given by, for example, Born (1926), Weisskopf (1931), Heitler (1954) pp. 138, 172, Shirley (1965b), Bates (1967), Ritus (1967), Zel'dovich (1967), and Young, Deal, and Kestner (1969).

[11] Theoretical discussions of those aspects of level shifts which are related to recent experiments are given by Barratand and Cohen-Tannoudji (1961a, b), Cohen-Tannoudji and Kastler (1966), Kastler (1963), Pancharatham (1966), Happer and Mathur (1967a), Bonch-Bruevich and Khodovoi (1968), Mathur, Tang, and Happer (1968).

the Dirac variation-of-constants solution for an arbitrary perturbation is not available.[12]

Although the question of secular terms is an old one in quantum mechanics, confusion over its proper resolution persists and periodically gives rise to "new" formulations of time-dependent perturbation theory.[13] Apparent differences between the static limits of the time-dependent perturbation equations and the customary time-independent equations are related to the presence of secular terms in the perturbation solution.[9] The recent variational formulations of time-dependent perturbation theory have refocused attention on the secular terms.[14] Difficulties from time-divergent terms can also arise in the construction of a unified variational principle for the time-dependent Schrödinger equation,[15] and a proper interpretation of secular terms and their source is essential for obtaining consistent and nonparadoxical results for the first- and higher-order transition rates induced by an applied perturbation.[16]

In addition to the apparent difficulties resulting from the presence of secular terms in the perturbation expansion of the wave function, its incorrect normalization can also be a source of error. If the Schrödinger equation is treated as an initial value problem and the Hamiltonian is a continuous function of the time, the Hermitian nature of the Hamiltonian insures that the time-dependent wave function is normalized at all times.[17] Incorrectly normalized wave functions can result, however, unless care is exercised in enforcing the initial conditions, or unless the required normalization terms are added in an *ad hoc* manner. In order to avoid this difficulty, it is convenient to identify the presence of an over-all multiplicative, time-dependent normalization factor in the wave function for a general perturbation, and to separate it from the wave function to all orders in perturbation theory. Such a normalization factor can, in fact, be formally related to the presence of secular terms and both aspects of the wave function treated on a common basis.

Although variational formulations of time-dependent perturbation theory suitable for computation have been described previously, primarily on an order-by-order basis,[7] there has been little discussion of their relation to the general variational principle of Frenkel and Dirac.[18] As we shall show, the Frenkel variational principle with a trial wave function in which the secular and normalization terms are written out explicitly, can be employed to unify the different variational procedures. There results a variational expression which, although not necessarily furnishing computattional advantages over the order-by-order approach, provides additional insights into the nature of the variational principles. In particular, the bounds to optical susceptibilities obtained for an harmonic perturbation from the order-by-order developments[7,8] are shown to follow directly from the Frenkel principle. That is, while the original Frenkel principle is not based on setting the variation of a functional equal to zero, the result we obtain from it has such a form and can furnish a bound to the system level shift induced by an oscillatory perturbation.[10] Further, the expression obtained from the Frenkel principle with explicit secular and normalization terms yields the familiar Ritz principle in the static limit.

The general interest in time-dependent problems and particularly the current concern with nonlinear optical phenomena suggests that a review of certain features of the Dirac perturbation method and its variational analogs is in order. Most important, explicit consideration of both normalization and secular terms appears to be needed. For this purpose, we consider the behavior of a nondegenerate system in the presence of an arbitrary time-dependent perturbation, focusing particular attention on the nonresonant case, although the formalism is applicable to transitions as well, and will be considered subsequently elsewhere. We demonstrate that an over-all time-dependent factor incorporating both the proper normalization and a phase factor arising from the eigenvalue perturbation can be separated multiplicatively from the total wave function. It is the perturbation expansion of this combined normalization and phase factor that gives rise to normalization and secular terms in the perturbation functions obtained from the Dirac variation-of-constant method. Moreover, we identify the normalization and phase factor as the amplitude for finding the system in the initial unperturbed state at any time $t$, and show that it can be

[12] The designation "secular term" is used here to describe any term, not necessarily time-divergent, which arises from the expansion of an over-all time-dependent phase in the wave function and which, consequently, does not contribute to the expectation value of an Hermitian operator. For historical reasons, it is apparently more common practice to associate this designation with terms which are time divergent. Our usage of the word secular is based on its meaning, "as opposed to regular"; as we shall see, the secular terms generally exhibit a time dependence which, though not necessarily time divergent, differs from that of the remaining regular part of the wave function.

[13] Such alternative formulations, when properly executed, are in fact equivalent to the original Dirac approach. See, for example, the recent formulations of Ezawa (1963) p. 93, and Chung (1967). The latter paper suggests that the customary Dirac approach is invalid in the static case, and that the time-dependent perturbation equations do not reduce to the familiar time-independent equations in the static limit. This erroneous observation is simply due to a failure to include the necessary secular terms in the time-dependent perturbation functions, as indicated in Footnote 9.

[14] The interesting gauge transformation approach to time-dependent problems described by Musher (1964) has emphasized that the ansatz used in writing out explicit forms for time-dependent variational wave functions can be incomplete unless the appropriate secular terms are properly included.

[15] A variational principle that provides a unification of previously described variation-perturbation approaches has been given recently by Heinrichs (1968a, b), who also deals successfully with features of the secular problem which arise in the variational formulation.

[16] A particularly clear account of the proper perturbative treatment of transition rates is given by Hammer and Weber (1965).

[17] See, for example, Messiah (1966), Vol. I, p. 119, for discussion of the conservation of the norm of the wave function.

[18] The variational principle generally attributed to Frenkel (1934) p. 253, is employed by Dirac (1930) in deriving the time-dependent Hartree–Fock equations. Frenkel points out that the principle first appeared in an Appendix to the Russian version of Dirac's well-known text.

obtained separately from the remaining "regular" portion of the wave function. The regular portion of the wave function remaining after extraction of the normalization and phase factor is expressed in a perturbation expansion. The resulting perturbation equations, which are distinct in form from the customary equations of time-dependent perturbation theory, are ideally suited for a variety of computational applications. As an alternative, we also write an additional set of perturbation functions which incorporate the normalization terms in expanded form, but which retain the secular terms in the over-all multiplicative phase factor. Finally, the total time-dependent perturbation functions, incorporating both secular and normalization terms, are obtained by a simultaneous perturbation expansion of the regular part of the wave function and the normalization and phase factor. The three different perturbation schemes are, of course, equivalent and if correctly treated yield, as they must, the same expectation values for Hermitian operators. All three perturbation expansions for the wave function can be obtained from the Dirac variation-of-constants method, which provides a correct solution of the time-dependent Schrödinger equation. Moreover, we emphasize that no formal difficulties or convergence problems ensue as a consequence of retaining the secular and normalization terms in the time-dependent perturbation functions. Our identification and extraction of such terms into over-all multiplicative factors is motivated primarily by the desire to correctly formulate a set of equations suitable for computational applications, to clarify the behavior of time-dependent perturbation theory in the static limit, and to demonstrate that the Frenkel principle provides a variational procedure which unifies the previously described order-by-order variational formulations, furnishing a bound to the system level shift induced by an oscillatory perturbation.

The general formulation of the time-dependent perturbation problem is presented in Sec. II. In Sec. III, we present a number of illustrative applications of the formalism. In the case of a linearly perturbed harmonic oscillator, for which the Schrödinger equation can be solved exactly in closed form, the resulting wave function provides an explicit illustration of the presence of an over-all multiplicative normalization and phase factor. We also employ the general development for the analysis of static, harmonic, and electromagnetic perturbations, and derive the form of time-dependent perturbation theory in the Hartree–Fock approximation.[2] For a static perturbation, the equations for the regular part of the wave function reduce directly to the customary equations of time-independent perturbation theory. In the important harmonic case, the perturbation functions are given explicitly through third order and compared with the results obtained directly from the Dirac variation-of-constants method. This allows the identification of the terms in the Dirac approach which give rise to normalization and secular terms, and reinforces the conclusion that the factoring procedure we introduce here is simply a convenient regrouping of the variation-of-constants results. For the special harmonic problem of an electromagnetic perturbation in the uniform-electric-field approximation,[19] we obtain expressions for various nonlinear optical suceptibilities which differ somewhat from earlier results which neglected normalization terms.[2,6] We compare our formulation of time-dependent perturbation theory in the uncoupled Hartree–Fock approximation with those given previously in the literature and emphasize the importance of extracting the secular terms in this application.[20] In Sec. IV, connection is made with alternative methods of dealing with secular terms in perturbation theory, including a projection-operator technique,[21] additional time scales,[22] and averaging procedures,[23] which provide further insights into the nature of the secular terms. We also indicate the suitability of the alternative perturbation equations for solution employing a Fourier analysis of the time-dependent perturbation. The unified variational formulation is presented in Sec. V and explicit connection is made with order-by-order variational formulations and with the Ritz principle in the limit of a static perturbation. The general variational development is applied to the Hartree–Fock approximation and used to obtain expressions suitable for computational applications. In the concluding discussion in Sec. VI, we emphasize that a proper interpretation of the Dirac variation-of-constants method and the Frenkel variational principle, including careful treatment of the secular and normalization terms, provides correct and convenient solutions of time-dependent perturbation problems.

## II. TIME-DEPENDENT PERTURBATION THEORY

In this section we review the customary time-dependent perturbation theory and identify the normalization and secular terms that appear in each order of the Dirac variation-of-constants solution. We show that such terms arise from the expansion of over-all multiplicative, time-dependent normalization and phase factors in the Schrödinger wave function. These multiplicative factors are explicitly extracted from

[19] For discussion of the uniform-electric-field approximation, see, for example, Goppert-Mayer (1931).

[20] The so-called uncoupled Hartree–Fock approximation to time-dependent perturbation theory is discussed by Karplus and Kolker (1963b), Chung (1967), and Heinrichs (1968c).

[21] The projection operator technique for eliminating secular and normalization terms from the time-dependent perturbation functions was suggested by Karplus and Kolker (1963a). For similar use of a project ion operator in separating the "relevant" and "irrelevant" parts of an ensemble density in the Liouville equation, see Zwanzig (1960).

[22] Applications of the so-called multiple-time-scales perturbation theory in statistical and quantum mechanics are given by Frieman (1963), Sandri (1963a, b, 1965), Boldt and Sandri (1964), Sandri and Sullivan (1965), Montgomery and Ruijgrok (1965), Case (1966), Goldberg and Sandri (1967a, b), Lochak and Thiounn (1969), Brooks and Scarfone (1969), Coffey and Ford (1969), Sengupta (1970), Kummer (1971), and Orr and Ward (1971).

[23] Detailed general accounts of multiple-time-scales perturbation theory and averaging procedures are given by Krylov and Bogolyubov (1947) and Bogolyubov and Mitropolskii (1961).

the wave function so that only the regular portion remains to be determined by perturbation theory.

We begin with the time-dependent Schrödinger equation

$$[H^{(0)}(\mathbf{r})+H^{(1)}(\mathbf{r},t)-i\hbar(\partial/\partial t)]\Psi(\mathbf{r},t)=0, \quad (1)$$

where both the unperturbed Hamiltonian $H^{(0)}(\mathbf{r})$ and the time-dependent perturbation Hamiltonian $H^{(1)}(\mathbf{r},t)$ are Hermitian operators in the vector space of $H^{(0)}(\mathbf{r})$.[24] The vector $\mathbf{r}$ appearing in Eq. (1) and throughout is used to represent all the spatial and spin coordinates of the system. This notation is not meant to imply, however, that the Hamiltonian operators are necessarily simple multiplicative functions of coordinates and time. Rather, they are generally operators which do not commute with one another. The perturbation Hamiltonian $H^{(1)}(\mathbf{r},t)$ is written for convenience in the form

$$H^{(1)}(\mathbf{r},t)=f(t)\,V^{(1)}(\mathbf{r},t), \quad (2)$$

where $V^{(1)}(\mathbf{r},t)$ describes the perturbation of interest and $f(t)$ is an appropriate switching function, chosen to apply the perturbation in the desired fashion and to satisfy the general requirement

$$H^{(1)}(\mathbf{r},t\rightarrow-\infty)\rightarrow 0. \quad (3a)$$

We assume that the system is originally $(t\rightarrow-\infty)$ in a particular nondegenerate, normalized eigenstate $\phi_0^{(0)}(\mathbf{r})$ of the unperturbed Hamiltonian $H^{(0)}(\mathbf{r})$, with energy $E_0^{(0)}$,

$$\Psi(\mathbf{r},t\rightarrow-\infty)=\phi_0^{(0)}(\mathbf{r})\,\exp[(i\hbar)^{-1}E_0^{(0)}t]\equiv\Psi^{(0)}(\mathbf{r},t), \quad (3b)$$

and that the perturbation Hamiltonian is sufficiently smooth and continuous in time to insure that the perturbed wave function $\Psi(\mathbf{r},t)$ and its first time derivative are also continuous functions of the time.[25] The unperturbed wave function $\Psi^{(0)}(\mathbf{r},t)$ is normalized to unity

$$\langle\Psi^{(0)}\mid\Psi^{(0)}\rangle=1, \quad (3c)$$

so that $\Psi(\mathbf{r},t)$ is similarly normalized

$$\langle\Psi\mid\Psi\rangle=1, \qquad \text{all } t, \quad (4)$$

as a consequence of the assumed smoothness and Hermiticity of the total Hamiltonian.[17,26] The conventional bracket notation in Eqs. (3c) and (4) implies integration over all spatial and spin coordinates, but not over the time variable.

Solution of Eq. (1) is facilitated by introducing the wave function in the interaction picture $\Psi_I(\mathbf{r},t)$ according to the transformation[27]

$$\Psi(\mathbf{r},t)=R(\mathbf{r},t)\Psi_I(\mathbf{r},t) \quad (5a)$$

with

$$R(\mathbf{r},t)=\exp[(i\hbar)^{-1}H^{(0)}(\mathbf{r})t]. \quad (5b)$$

Substituting Eq. (5a) into Eq. (1) gives the Schrödinger equation in the interaction picture

$$[H_I^{(1)}(\mathbf{r},t)-i\hbar(\partial/\partial t)]\Psi_I(\mathbf{r},t)=0, \quad (6a)$$

where

$$H_I^{(1)}(\mathbf{r},t)=R^\dagger(\mathbf{r},t)H^{(1)}(\mathbf{r},t)R(\mathbf{r},t) \quad (6b)$$

is the transformed perturbation Hamiltonian and we employ the customary notation, $R^\dagger(\mathbf{r},t)$, for the adjoint of $R(\mathbf{r},t)$. A formal solution of Eqs. (6) can be written in the form

$$\Psi_I(\mathbf{r},t)=U(\mathbf{r},t)\Psi_I(\mathbf{r},-\infty)=U(\mathbf{r},t)\phi_0^{(0)}(\mathbf{r}), \quad (7)$$

where $U(\mathbf{r},t)$ is the time evolution operator,[27] satisfying the initial condition

$$U(\mathbf{r},-\infty)=\mathbf{1} \quad (8a)$$

and the unitary requirement

$$U^\dagger(\mathbf{r},t)\,U(\mathbf{r},t)=U(\mathbf{r},t)\,U^\dagger(\mathbf{r},t)=\mathbf{1}, \quad (8b)$$

with $\mathbf{1}$ the identity operator.

In certain instances, $U(\mathbf{r},t)$ can be obtained in closed form as an integral or differential operator, in which case the Schrödinger wave function is given directly by Eqs. (5) and (7).[28] More generally, an iterative perturbation approach, which is conveniently formulated in terms of the matrix elements of the time evolution operator in a particular basis set,[29] must be employed.

[24] We assume that the perturbation Hamiltonian $H^{(1)}(\mathbf{r},t)$ is a bounded operator in the separable Hilbert space of the unperturbed Hamiltonian $H^{(0)}(\mathbf{r})$, and restrict attention to the perturbation of a bound state. For discussion of questions relating to the existence of solutions of Eq. (1) and of the convergence of the associated perturbation expansions, which are important but not central to our development, see, for example, Friedrichs (1966), and references cited therein.

[25] By enforcing the initial conditions of Eqs. (3a) and (3b) in the infinite past, $t\rightarrow-\infty$, we do not mean to imply that the development is necessarily limited to the class of adiabatic perturbations. On the contrary, the appropriate choice of switching function $f(t)$ can provide a sudden perturbation, Pauli (1933), an adiabatic pertrubation, Born and Fock (1928), or any situation in between these two familiar limits. Clearly, the solution of Eq. (1) is generally dependent upon the specific switching function employed.

[26] The nature of the switching function employed is critical in this regard. For example, adiabatic switching carried out over a long but finite interval, such as that discussed by Bohm (1951) Chap. 18, does not give rise to the necessary normalization terms and, consequently, is unsatisfactory. See, for example, Sitz and Yaris (1968), where such switching is used to establish the adiabatic theorem in the static case, resulting in the secular terms explicitly to second-order, but omitting the normalization terms entirely and, consequently, violating Eq. (4). The step function switching originally employed by Dirac (1926) can be introduced in this approach as the limit of an initially continuous switching function. In this manner, sudden switching is achieved and the normalization of the wave function is insured, as well. Further discussion of specific switching functions is given in Sec. III.

[27] See, for example, Roman (1965) p. 49, for discussion of the interaction picture.

[28] A particularly convenient form for the time evolution operator, that automatically preserves unitarity and in terms of which most solvable problems can be expressed, is given by Magnus (1954), and is discussed particularly clearly by Pechukas and Light (1966).

[29] Perturbation theory can also be formulated directly in terms of the time evolution operator. See, for example, Dyson (1949), Feynman (1951), and Roman (1965), p. 49. It is worth noting that in certain instances the time evolution operator may exist but its expansion in terms of matrix elements in a particular basis set may not necessarily converge.

### A. Variation of Constants

Explicit expressions for the elements of the time evolution operator are provided by the customary Dirac variation-of-constants procedure.[1] This technique introduces the spectral expansion

$$\Psi_I(\mathbf{r}, t) = \sum_{k=0}^{\infty} a_k(t)\phi_k^{(0)}(\mathbf{r}), \tag{9}$$

where the functions $\phi_k^{(0)}(\mathbf{r})$ are the orthonormal eigenstates of the unperturbed Hamiltonian.[30] Employing the expression [Eq. (9)] in the Schrödinger equation [Eqs. (6)] gives the familiar result

$$\partial a_k(t)/\partial t = (i\hbar)^{-1}\sum_{l=0}^{\infty}\langle\phi_k^{(0)} \mid H_I^{(1)} \mid \phi_l^{(0)}\rangle a_l(t), \tag{10a}$$

$$a_k(t) = \delta_{k0} + (i\hbar)^{-1}\int_{-\infty}^{t}\sum_{l=0}^{\infty}\langle\phi_k^{(0)} \mid H_I^{(1)} \mid \phi_l^{(0)}\rangle a_l(t')\, dt', \tag{10b}$$

for the expansion coefficients $a_k(t)$, where we have introduced the initial conditions of Eqs. (3). These coefficients are the desired matrix elements of the $U$-matrix operator, since we have

$$a_k(t) = \langle\phi_k^{(0)} \mid \Psi_I\rangle = \langle\phi_k^{(0)} \mid U \mid \phi_0^{(0)}\rangle \tag{11}$$

from Eqs. (7) and (9). It is an immediate consequence of Eqs. (10) that

$$\frac{\partial}{\partial t}\sum_{k=0}^{\infty} \mid a_k(t)\mid^2 = 0, \tag{12a}$$

and the initial conditions of Eqs. (3) insure that [Eq. (4)]

$$\sum_{k=0}^{\infty} \mid a_k(t)\mid^2 = 1. \tag{12b}$$

Equation (12b) also follows from Eq. (11) employing closure, the unitarity of $U(\mathbf{r}, t)$, and the fact that $\phi_0^{(0)}(\mathbf{r})$ is normalized to unity.

Following the customary development, Eqs. (10) are solved employing the perturbation expansion

$$a_k(t) = \sum_{n=0}^{\infty} a_k^{(n)}(t), \tag{13a}$$

with the requirements

$$a_k^{(0)}(t) = \delta_{k0}, \tag{13b}$$

$$a_k^{(n)}(t \to -\infty) = 0, \qquad n \neq 0, \tag{13c}$$

which insure that the initial conditions [Eqs. (3)] can be satisfied independently of the strength of the perturbation. We obtain the familiar coupled equations

$$\partial a_k^{(n)}(t)/\partial t = (i\hbar)^{-1}\sum_{l=0}^{\infty}\langle\phi_k^{(0)} \mid H_I^{(1)} \mid \phi_l^{(0)}\rangle a_l^{(n-1)}(t) \qquad n>0, \tag{14a}$$

$$a_k^{(n)}(t) = (i\hbar)^{-1}\int_{-\infty}^{t}\sum_{l=0}^{\infty}\langle\phi_k^{(0)} \mid H_I^{(1)} \mid \phi_l^{(0)}\rangle a_l^{(n-1)}(t')\, dt' \qquad n>0, \tag{14b}$$

which can be employed to determine the $a_k(t)$ coefficients to arbitrarily high order by carrying out the indicated quadratures, starting with the first approximation in Eq. (13b).

It is also convenient to introduce the perturbation functions

$$\Psi_I^{(n)}(\mathbf{r}, t) = \sum_{k=0}^{\infty} a_k^{(n)}(t)\phi_k^{(0)}(\mathbf{r}), \tag{15}$$

in terms of which the wave function in the interaction picture is given by the perturbation expansion

$$\Psi_I(\mathbf{r}, t) = \sum_{n=0}^{\infty}\Psi_I^{(n)}(\mathbf{r}, t). \tag{16}$$

The corresponding functions $\Psi^{(n)}(\mathbf{r}, t)$ in the Schrödinger picture are

$$\Psi^{(n)}(\mathbf{r}, t) = R(\mathbf{r}, t)\Psi_I^{(n)}(\mathbf{r}, t) = \sum_{k=0}^{\infty} a_k^{(n)}(t)\phi_k^{(0)}(\mathbf{r})\exp[(i\hbar)^{-1}E_k^{(0)}t], \tag{17}$$

and the complete Schrödinger wave function $\Psi(\mathbf{r}, t)$ is given by the perturbation expansion

$$\Psi(\mathbf{r}, t) = \sum_{n=0}^{\infty}\Psi^{(n)}(\mathbf{r}, t). \tag{18}$$

The time-dependent perturbation functions, $\Psi^{(n)}(\mathbf{r}, t)$, are solutions of the equations

$$[H^{(0)}(\mathbf{r}) - i\hbar(\partial/\partial t)]\Psi^{(0)}(\mathbf{r}, t) = 0, \tag{19a}$$

$$[H^{(0)}(\mathbf{r}) - i\hbar(\partial/\partial t)]\Psi^{(n)}(\mathbf{r}, t) + H^{(1)}(\mathbf{r}, t)\Psi^{(n-1)}(\mathbf{r}, t) = 0 \qquad n>0, \tag{19b}$$

and, if an appropriate switching function is employed, satisfy *identically* the normalization conditions

$$\sum_{k=0}^{n}\langle\Psi^{(k)} \mid \Psi^{(n-k)}\rangle = 0 \qquad n>0, \tag{19c}$$

as a consequence of Eqs. (3) and (4).

In obtaining the perturbation functions $\Psi^{(n)}(\mathbf{r}, t)$ [Eq. (17)], we have employed here the spectral expansion of Eq. (9) and the subsequent perturbation expansion of Eqs. (13). Alternatively, we can insert the perturbation expansion of Eq. (18) into Eq. (1) in order to obtain the sequence of perturbation equations satisfied by the $\Psi^{(n)}(\mathbf{r}, t)$ [Eqs. (19)], without recourse to a spectral expansion. The two procedures are, of course, identical, and subsequent substitution of expansions in the form of Eq. (17) into Eqs. (19) results

[30] The completeness of this set in the vector space of the total Hamiltonian in the case of quantum electrodynamic interactions has been questioned by Dirac (1965). We no not consider such a question here but, rather, assume the necessary completeness and the convergence of the expansion in Eq. (9).

in the $a_k^{(n)}(t)$ of Eqs. (14). It is important to recognize, however, that the spectral expansion is not necessary for a perturbative solution of the Schrödinger equation.

The foregoing formal procedure is complete and well known and there is nothing additional required for its implementation, other than an examination of its convergence for specific perturbations.[31] To clarify certain complications that can arise, however, it is useful to extract from the perturbation functions $\Psi^{(n)}(\mathbf{r}, t)$ of Eq. (17) the terms which insure that the total wave function [Eq. (18)] is correctly normalized and those which arise from the expansion of an over-all time-dependent phase in the wave function. The presence of terms in the perturbation functions which insure that the complete wave function is correctly normalized to each order in the perturbation is suggested by Eq. (19c), while the appearance of secular terms in the $\Psi^{(n)}(\mathbf{r}, t)$ of Eq. (17) is expected, in part, on basis of the form which the perturbation functions take in the limit of a static perturbation.[9] The secular terms, which need not necessarily be time divergent, can also be identified by an order-by-order treatment of Eqs. (14) and (17), although such a development becomes tedious in higher orders.[32] In this connection, it is helpful to recognize that in the static case it is customary to extract the secular divergences in the form of an overall phase factor involving the perturbed energy eigenvalue, thus bypassing Eqs. (19). We can anticipate that a similar procedure will be successful in extracting the more general secular terms that arise from a time-dependent phase in the wave function for an arbitrary time-dependent perturbation. Such secular terms, since they arise from the expansion of an over-all phase, will not contribute to the expectation values of physical observables, cancelling identically in each order of perturbation theory.[33] The normalization terms, which do contribute to expectation values, can be written most conveniently in a form which makes explicit their presence and insures that they are included correctly. When the secular and normalization terms have been explicitly extracted, it is possible to focus attention on the remaining regular part of the wave function.

### B. Secular and Normalization Terms

Our development is predicated on the isolation of a multiplicative time-dependent factor in the total wave function [Eq. (18)] that contains an over-all phase factor and a term providing for the correct normalization of the wave function. We can accomplish this most directly by writing the wave function in the interaction picture in the form

$$\Psi_I(\mathbf{r}, t) = a_0(t)[\phi_0^{(0)}(\mathbf{r}) + \sum_{k\neq 0}^{\infty} b_k(t)\phi_k^{(0)}(\mathbf{r})], \quad (20a)$$

where

$$b_k(t) \equiv a_k(t)/a_0(t). \quad (20b)$$

This particular factoring of the coefficients $a_k(t)$ is legitimate as long as $a_0(t)$ is well behaved, and does not limit the generality of our procedure. Moreover, in view of the initial condition of Eqs. (3b) and (13b), the coefficient $a_0(t)$ is the only one that can be factored from the wave function and give well-behaved $b_k(t)$ in the limit $t\to-\infty$. The Schrödinger wave function now takes the form

$$\Psi(\mathbf{r}, t) = a_0(t)\phi(\mathbf{r}, t)\ \exp[(i\hbar)^{-1}E_0^{(0)}t], \quad (21)$$

where we have introduced the function

$$\phi(\mathbf{r}, t) \equiv \phi_0^{(0)}(\mathbf{r}) + \sum_{k\neq 0}^{\infty} b_k(t)\phi_k^{(0)}(\mathbf{r}) \times \exp[(i\hbar)^{-1}(E_k^{(0)} - E_0^{(0)})t], \quad (22)$$

which satisfies the "intermediate" normalization condition[34]

$$\langle\phi_0^{(0)} \mid \phi\rangle = \langle\phi_0^{(0)} \mid \phi_0^{(0)}\rangle = 1, \quad (23)$$

with $\phi_0^{(0)}(\mathbf{r})$ the unperturbed eigenstate. From Eqs. (21) and (23) we see that $a_0(t)$ has the form

$$a_0(t) = \langle\Psi^{(0)} \mid \Psi\rangle, \quad (24)$$

[31] The boundedness of $H^{(1)}(\mathbf{r}, t)$ is generally required to insure convergence. See, for example, Kato (1949), Hammer and Weber (1965), Sasakawa (1966), and Simon (1971), where questions of convergence are explicitly examined.

[32] It is a simple matter, however, to identify the secular terms which appear in the lower-order functions. From Eqs. (14) and (17), we see that the first-order perturbation function can be written in the form

$$\Psi^{(1)}(\mathbf{r}, t) = [\phi^{(1)}(\mathbf{r}, t) + (i\hbar)^{-1}\int_{-\infty}^{t} \langle\phi_0^{(0)} \mid H_I^{(1)} \mid \phi_0^{(0)}\rangle\, dt' \times\phi_0^{(0)}(\mathbf{r})]\exp[(i\hbar)^{-1}E_0^{(0)}t],$$

where $\phi^{(1)}(\mathbf{r}, t)$ is a function comprising all the terms in Eq. (17) $[n=1]$ orthogonal to $\phi_0^{(0)}(\mathbf{r})$. Since the term in $\Psi^{(1)}(\mathbf{r}, t)$ proportional to $\phi_0^{(0)}(\mathbf{r})$ is a purely imaginary (secular) term, it is clear that the complete wave function, to first order, can be written in the form

$$\Psi(\mathbf{r}, t) = [\phi_0^{(0)}(\mathbf{r}) + \phi^{(1)}(\mathbf{r}, t) + \cdots]\exp[(i\hbar)^{-1}(E_0^{(0)}t + \int_{-\infty}^{t} \langle\phi_0^{(0)} \mid H_I^{(1)} \mid \phi_0^{(0)}\rangle dt' + \cdots)].$$

Moreover, in the limit of a static perturbation, the second term in the exponential becomes the first-order level shift factor $(i\hbar)^{-1}E_s^{(1)}t$, and $\phi^{(1)}(\mathbf{r}, t)$ becomes the first-order static perturbation function $\chi_s^{(1)}(\mathbf{r})$. Similarly, in second order the secular terms can be picked out of the solution of Eqs. (14) and (17) and also combined into an over-all, time-dependent phase factor, as we shall demonstrate explicitly in Sec. III.C. In this connection, it is important to recognize that although the development of Eqs. (9)–(19) results in a unique time-dependent phase factor in the wave function, it is always possible, by the addition of an arbitrary real constant to the phase, to obtain a modified wave function that is also a solution of the Schrödinger equation. The connection between this familiar "gauge invariance" and an apparent indeterminancy in the time-dependent perturbation functions—the possibility of adding an arbitrary (constant) imaginary multiple of the unperturbed wave function to the solution of Eq. (19b)—is discussed in Sec. II.C.

[33] For any operator $A(\mathbf{r}, t)$ not containing time derivatives, it is clear that $\langle\Psi \mid A \mid \Psi\rangle = \langle\theta \mid A \mid \theta\rangle$ when $\Psi(\mathbf{r}, t) = \theta(\mathbf{r}, t)\times \exp[ig(t)]$, where $g(t)$ is real. The time derivative $\partial/\partial t$ is not an Hermitian operator in the space of functions $\phi_k^{(0)}(\mathbf{r})$, and its expectation value $\langle\Psi \mid \partial/\partial t \mid \Psi\rangle = ig(t) + \langle\theta \mid \partial/\partial t \mid \theta\rangle$ involves the phase factor $g(t)$. However, the Hermitized form $T(t) = \frac{1}{2}[(\partial/\partial t) + (\partial/\partial t)^\dagger]$ where the adjoint $(\partial/\partial t)^\dagger$ satisfies $\langle\Psi \mid (\partial/\partial t)^\dagger \mid \Psi\rangle = \langle\Psi \mid \partial/\partial t \mid \Psi\rangle^*$, clearly gives $\langle\Psi \mid T \mid \Psi\rangle = \langle\theta \mid T \mid \theta\rangle$. Similar results apply to the higher-order time derivatives. Consequently, the expectation values of *Hermitian* operators containing time derivatives are also independent of the phase factor $g(t)$.

[34] The function $\phi(\mathbf{r}, t)$ is evidently the portion of the wave function which satisfies intermediate normalization, similar to that introduced in the static case by Bloch (1958a, b).

which we identify as the amplitude for finding the system in the initial unperturbed state at any time $t$. In view of the form of the function $\phi(\mathbf{r}, t)$ [Eq. (22)], it is perfectly clear that any over-all multiplicative, time-dependent factor in the wave function must be incorporated in the amplitude $a_0(t)$ of Eq. (24).

It is a simple matter to demonstrate that the multiplicative factor of Eq. (24) incorporates the secular and normalization terms in the static limit, with $H^{(1)}(\mathbf{r}, t)$ independent of $t$ for $t\rightarrow+\infty$. In this case, the adiabatic theorem is used to show that for $t\rightarrow+\infty$ the time-dependent wave function is of the form[35]

$$\Psi_s(\mathbf{r}, t)=\chi_s(\mathbf{r})\exp\left[(i\hbar)^{-1}E_s t\right], \tag{25}$$

where $\chi_s(\mathbf{r})$ is the normalized eigenfunction of the total Hamiltonian, $H^{(0)}(\mathbf{r})+H^{(1)}(\mathbf{r})$, obtained from $\phi_0^{(0)}(\mathbf{r})$ using time-independent perturbation theory for the perturbation $H^{(1)}(\mathbf{r})$, and the quantity $E_s$ is the corresponding perturbed eigenvalue. From Eqs. (24) and (25) it follows that for $t\rightarrow+\infty$ we have

$$a_0(t)=\langle\Psi^{(0)}\mid\Psi_s\rangle=\langle\phi_0^{(0)}\mid\chi_s\rangle\exp\left[(i\hbar)^{-1}(E_s-E_0^{(0)})t\right]. \tag{26}$$

Consequently, in the static limit the partitioning [Eq. (21)] is equivalent to the customary ansatz [Eq. (25)] for isolating the phase factor that arises from the system level shift. Moreover, in the static case, the function $\phi(\mathbf{r}, t)$ is of the form

$$\phi_s(\mathbf{r})=\chi_s(\mathbf{r})\langle\phi_0^{(0)}\mid\chi_s\rangle^{-1} \tag{27}$$

from Eqs. (21), (25), and (26), which we recognize as the static wave function in intermediate normalization. Consequently, the proper normalization factor $\langle\phi_0^{(0)}\mid\chi_s\rangle$ is contained in $a_0(t)$ [Eq. (26)], as well.

To investigate the nature of the factoring of the wave function for a general time-dependent perturbation, we substitute Eq. (21) into Eq. (1), multiply by $\phi_0^{(0)}(\mathbf{r}, t)^*$, and integrate over the coordinates. This procedure gives separate equations for $a_0(t)$

$$\partial a_0(t)/\partial t=(i\hbar)^{-1}\Delta E(t)\,a_0(t), \tag{28a}$$

and for $\phi(\mathbf{r}, t)$

$$\left[H^{(0)}(\mathbf{r})-E_0^{(0)}-i\hbar(\partial/\partial t)\right]\phi(\mathbf{r}, t)+\left[H^{(1)}(\mathbf{r}, t)-\Delta E(t)\right]\phi(\mathbf{r}, t)=0, \tag{28b}$$

with

$$\Delta E(t)=\langle\phi_0^{(0)}\mid H^{(1)}\mid\phi\rangle, \tag{28c}$$

or

$$E_0^{(0)}+\Delta E(t)=\langle\phi\mid H^{(0)}+H^{(1)}-i\hbar(\partial/\partial t)\mid\phi\rangle\langle\phi\mid\phi\rangle^{-1}. \tag{28d}$$

Equation (28a) can also be obtained from Eqs. (10) for $k=0$, employing the definition of the function $\phi(\mathbf{r}, t)$ [Eq. (22)]. Making use of the initial condition $a_0(t\rightarrow-\infty)=1$ from Eqs. (3), we can integrate Eq. (28a) to obtain

$$a_0(t)=\exp\left((i\hbar)^{-1}\int_{-\infty}^{t}\Delta E(t')\,dt'\right). \tag{29}$$

[35] See, for example, Messiah (1966), Chap. 17, Secs. 10–13, for discussion of the adiabatic theorem.

Equations (28c) and (29) show that $a_0(t)$ is obtained from the function $\phi(\mathbf{r}, t)$ as, consequently, is the complete time-dependent wave function $\Psi(\mathbf{r}, t)$ [Eq. (21)].[36] The quantity $\Delta E(t)$ defined in Eqs. (28c) and (28d) is, in general, both complex and time-dependent. From Eqs. (24), (28), and (29), it follows that $\Delta E(t)$ can also be written in the forms

$$\Delta E(t)=i\hbar(\partial/\partial t)(\ln\langle\Psi^{(0)}\mid\Psi\rangle)=\langle\Psi^{(0)}\mid H^{(1)}\mid\Psi\rangle/\langle\Psi^{(0)}\mid\Psi\rangle. \tag{28e}$$

We now show that the imaginary part of $\Delta E(t)$ insures that the wave function of Eq. (21) is properly normalized for all $t$ and that the real part of $\Delta E(t)$ gives rise to an over-all phase factor that contains the system level shift. Multiplying Eq. (28b) by $\phi(\mathbf{r}, t)^*$, integrating over the coordinates, and subtracting the complex conjugate of the resulting equation from the equation itself, we find

$$\hbar(\partial/\partial t)\langle\phi\mid\phi\rangle=-2\langle\phi\mid\phi\rangle\,\mathrm{Im}\,\Delta E(t). \tag{30}$$

This expression can be integrated to give

$$\langle\phi\mid\phi\rangle^{-1/2}=\exp\left((\hbar)^{-1}\int_{-\infty}^{t}\mathrm{Im}\,\Delta E(t')\,dt'\right), \tag{31}$$

where we have made use of the initial condition, $\langle\phi\mid\phi\rangle\rightarrow1$, $t\rightarrow-\infty$, obtained directly from Eqs. (3). Thus we find

$$a_0(t)=\langle\Psi^{(0)}\mid\Psi\rangle=\exp\left((i\hbar)^{-1}\int_{-\infty}^{t}\Delta E(t')\,dt'\right)=\langle\phi\mid\phi\rangle^{-1/2}\exp\left((i\hbar)^{-1}\int_{-\infty}^{t}\mathrm{Re}\,\Delta E(t')\,dt'\right) \tag{32}$$

and see that the total wave function [Eq. (21)] has the form

$$\Psi(\mathbf{r}, t)=\phi(\mathbf{r}, t)\langle\phi\mid\phi\rangle^{-1/2}\times\exp\left[(i\hbar)^{-1}\left(E_0^{(0)}t+\int_{-\infty}^{t}\mathrm{Re}\,\Delta E(t')\,dt'\right)\right]. \tag{33}$$

Equations (31)–(33) demonstrate that $\mathrm{Im}\,\Delta E(t)$ does indeed insure that the total wave function is properly normalized for all $t$, since the phase factor appearing in Eq. (33) is purely imaginary. Moreover, from Eqs. (31) and (32) we have

$$|a_0|^2=|\langle\Psi^{(0)}\mid\Psi\rangle|^2=\exp\left(2(\hbar)^{-1}\int_{-\infty}^{t}\mathrm{Im}\,\Delta E(t')\,dt'\right)=\langle\phi\mid\phi\rangle^{-1}, \tag{34}$$

[36] To emphasize that Eq. (21) is simply a particular rearrangement of the variation-of-constants solution [Eqs. (5) and (9)], we note that the solution of Eqs. (28) in the form of a spectral expansion, when employed in Eq. (21), recovers the Dirac solution [Eqs. (5) and (9)], with $a_k(t)$ given by Eqs. (10). The particular advantages that derive from the factoring of the wave function employed in Eq. (21), which results in Eqs. (28), will become clear from the subsequent discussion of the solution of Eq. (28b).

emphasizing the intimate connection between the modulus of $\langle\Psi^{(0)} \mid \Psi\rangle$ and the normalization of the wave function. We can also obtain Eq. (34) directly from the normalization condition of Eqs. (12) and the definition of $\phi(\mathbf{r}, t)$ [Eq. (22)].

In order to determine the physical significance of Re $\Delta E(t)$, we employ Eqs. (28c) and (28e) to obtain

$$\begin{aligned}\text{Re } \Delta E(t) &= \text{Re } \langle\phi_0^{(0)} \mid H^{(1)} \mid \phi\rangle \\ &= \text{Re } [\langle\Psi^{(0)} \mid H^{(1)} \mid \Psi\rangle / \langle\Psi^{(0)} \mid \Psi\rangle], \quad (35)\end{aligned}$$

which is analogous to the familiar level shift expression in the static case.[37] It is easy to see, however, that $E_0^{(0)}+$ Re $\Delta E(t)$ is generally not the expectation value of the total time-dependent Hamiltonian for the total wave function. To demonstrate this, and to examine the consequences, we introduce the function

$$\chi(\mathbf{r}, t) = \phi(\mathbf{r}, t)\,\langle\phi \mid \phi\rangle^{-1/2} \quad (36)$$

which satisfies the normalization condition

$$\langle\chi \mid \chi\rangle = 1. \quad (37)$$

From Eqs. (23) and (36) we have

$$\langle\phi_0^{(0)} \mid \chi\rangle = \langle\phi \mid \phi\rangle^{-1/2} \quad (38)$$

and, consequently, $\phi(\mathbf{r}, t)$ can be written as

$$\phi(\mathbf{r}, t) = \chi(\mathbf{r}, t)\,\langle\phi_0^{(0)} \mid \chi\rangle^{-1}, \quad (39)$$

analogous to the static wave function in intermediate normalization [Eq. (27)]. The complete wave function [Eq. (33)] when written in terms of $\chi(\mathbf{r}, t)$ is simply

$$\Psi(\mathbf{r}, t) = \chi(\mathbf{r}, t) \times \exp\left[(i\hbar)^{-1}\left(E_0^{(0)}t + \int_{-\infty}^{t} \text{Re } \Delta E(t')\, dt'\right)\right]. \quad (40)$$

We obtain a differential equation for $\chi(\mathbf{r}, t)$ by substituting Eq. (36) into Eq. (28b), or, equivalently, substituting Eq. (40) into Eq. (1). This procedure gives

$$[H^{(0)}(\mathbf{r}) - E_0^{(0)} - i\hbar(\partial/\partial t)]\chi(\mathbf{r}, t) + [H^{(1)}(\mathbf{r}, t) - \text{Re } \Delta E(t)]\chi(\mathbf{r}, t) = 0, \quad (41a)$$

with

$$\text{Re } \Delta E(t) = (\langle\chi^{(0)} \mid H^{(1)} \mid \chi\rangle - i\hbar\langle\chi^{(0)} \mid \partial\chi/\partial t\rangle) \times \langle\chi^{(0)} \mid \chi\rangle^{-1}. \quad (41b)$$

The equivalence of Eq. (41b), which is obtained from Eq. (41a) by multiplying by $\chi^{(0)}(\mathbf{r})^*[=\phi_0^{(0)}(\mathbf{r})^*]$ and integrating over the coordinates, with Eq. (35), can be demonstrated by employing the definition of $\chi(\mathbf{r}, t)$ [Eq. (36)]. An alternative expression for Re $\Delta E(t)$ is obtained from Eq. (41a) by multiplying by $\chi(\mathbf{r}, t)^*$ and integrating over coordinates, giving

$$E_0^{(0)} + \text{Re } \Delta E(t) = \langle\chi \mid H^{(0)} + H^{(1)} - i\hbar(\partial/\partial t) \mid \chi\rangle \quad (42)$$

where we have employed the normalization condition of Eq. (37). Alternatively, Eq. (42) results from substituting Eq. (39) into Eq. (28d) and isolating its real part.

Since the Hamiltonian operator is Hermitian, we have[33]

$$\langle\chi \mid H^{(0)} + H^{(1)} \mid \chi\rangle = \langle\Psi \mid H^{(0)} + H^{(1)} \mid \Psi\rangle, \quad (43)$$

and Eq. (42) becomes

$$\begin{aligned}E_0^{(0)} + \text{Re } \Delta E(t) &= \langle\Psi \mid H^{(0)} + H^{(1)} \mid \Psi\rangle - i\hbar\langle\chi \mid \partial\chi/\partial t\rangle \\ &= i\hbar\langle\Psi \mid \partial\Psi/\partial t\rangle - i\hbar\langle\chi \mid \partial\chi/\partial t\rangle, \quad (44)\end{aligned}$$

demonstrating that $E^{(0)}+$ Re $\Delta E(t)$ is, in general, not the expectation value of the total time-dependent Hamiltonian.[38] However, for a simply periodic perturbation, $H^{(1)}(\mathbf{r}, t) = H^{(1)}(\mathbf{r}, t+\tau)$, or for the individual Fourier components of a more general time-dependent perturbation, we anticipate that Eq. (44) will incorporate a time-independent term, $\Delta E$, which can be interpreted as the mean energy level shift of the system.[10] That is, for a simply periodic perturbation, we can expect solutions of the Schrödinger equation to take the form of quasiperiodic states,[39]

$$\begin{aligned}\Psi(\mathbf{r}, t) &= \chi(\mathbf{r}, t)\, \exp\left((i\hbar)^{-1}[(E_0^{(0)} + \Delta E)t + \int_{-\infty}^{t} (\text{Re } \Delta E(t') - \Delta E)\, dt']\right) \\ &\equiv \theta(\mathbf{r}, t)\, \exp\,[(i\hbar)^{-1}(E_0^{(0)} + \Delta E)t], \quad (45)\end{aligned}$$

[37] See, for example, Goldstone (1957).

[38] This serves to emphasize that the solutions of Eq. (41a) are generally not the instantaneous eigenstates introduced by Born and Fock (1928). However, in the special case of an adiabatically switched-on static perturbation, when the time derivative in Eq. (41a) can be neglected, the solutions do become the Born–Fock eigenstates.

[39] This form of wave function [Eqs. (45) and (46)] is analogous to the familiar Bloch waves which arise in electron band theory for a spatially periodic potential. Shirley (1965a) has recently emphasized that the solutions of Eq. (1) for a periodic Hamiltonian $H(\mathbf{r}, t+\tau) = H(\mathbf{r}, t)$ in a finite dimensional Hilbert space are also of the form $\Psi(\mathbf{r}, t) = \theta(\mathbf{r}, t)\, \exp\,[(i\hbar)^{-1}Et]$, where $E$ is a real constant, and $\theta(\mathbf{r}, t+\tau) = \theta(\mathbf{r}, t)$, as a consequence of the Floquet theorem. Such states are designated quasiperiodic by Young, Deal, and Kestner (1969), who give further discussion in the more general case of an infinite dimensional Hilbert space. For such quasiperiodic states, it is clear that the over-all phase factor in Eq. (40) must contain the level-shift term and, consequently, $\chi(\mathbf{r}, t)$ will be periodic. That is, aside from the periodic phase factor,

$$\exp\,[(i\hbar)^{-1}\int_{-\infty}^{t} (\text{Re } \Delta E(t') - \Delta E)\, dt'],$$

the functions $\theta(\mathbf{r}, t)$ and $\chi(\mathbf{r}, t)$ of Eq. (45) are identical. An alternative argument for the existence of solutions of Eq. (1) in the form of Eqs. (45) and (46) can be made by recognizing that the Schrödinger operator, $T(\mathbf{r}, t) \equiv [H(\mathbf{r}, t) - i\hbar(\partial/\partial t)]$, for a periodic perturbation is linear and Hermitian in the Hilbert space $a_k(t)\phi_k^{(0)}(\mathbf{r})$, where the $a_k(t)$ are square-integrable functions defined over the finite interval $0 \leq t \leq \tau$. Consequently, we can expect spectral solutions $[T(\mathbf{r}, t) - E_k]\theta_k(\mathbf{r}, t) = 0$ and associated functions $\Psi_k(\mathbf{r}, t) = \theta_k(\mathbf{r}, t)\, \exp\,[(i\hbar)^{-1}E_k t]$ to exist, where the $\theta_k(\mathbf{r}, t)$ and related functions $\phi_k(\mathbf{r}, t)$ or $\chi_k(\mathbf{r}, t)$ are of necessity periodic to insure the single valuedness of the wave function. The $\Psi_k(\mathbf{r}, t)$ so defined satisfy the Schrödinger equation $T(\mathbf{r}, t)\Psi_k(\mathbf{r}, t) = 0$ and provide an orthonormal set of states which describe the system's steady-state response to an external periodic perturbation. Moreover, under appropriate conditions, the "eigenstates" $\Psi_k(\mathbf{r}, t)$ can be placed in one-to-one correspondence with the $\Psi_k^{(0)}(\mathbf{r}, t)$ of the unperturbed system and provide a natural generalization in the time-dependent case of the more familiar static eigenfunctions. This particular perspective, based on square-integrable functions in the time domain, has been adopted by Okuniewicz (1972), who investigates in detail questions pertaining to the existence of solutions of the Schrödinger in the form of Eqs. (45) and (46). We thank Dr. Okuniewicz for correspondence and discussion and for providing us with results prior to publication.

where $\theta(\mathbf{r}, t)$ satisfies

$$[H^{(0)}(\mathbf{r})+H^{(1)}(\mathbf{r}, t)-i\hbar(\partial/\partial t)]\theta(\mathbf{r}, t) = (E_0^{(0)}+\Delta E)\theta(\mathbf{r}, t), \quad (46)$$

and is a periodic function of the time, $\theta(\mathbf{r}, t)=\theta(\mathbf{r}, t+\tau)$. In order to clarify the physical significance of the level shift, $\Delta E$, appearing in the phase factor of Eq. (45), we introduce an explicit perturbation parameter $\lambda$ into the development and write the Hamiltonian $H(\mathbf{r}, t; \lambda)$ and the wave function $\Psi(\mathbf{r}, t; \lambda)$ as explicit functions of this parameter. The time-dependent Hellmann–Feynman theorem can now be employed in the form[40]

$$\langle\Psi(\lambda)|\, H^{(1)} \,|\Psi(\lambda)\rangle = i\hbar(\partial/\partial t)\langle\Psi(\lambda)|\, \partial\Psi(\lambda)/\partial\lambda\rangle \quad (47)$$

to establish the physical significance of $\Delta E(\lambda)$. Introducing Eq. (40), with $\chi(\mathbf{r}, t; \lambda)$ and $\mathrm{Re}\,\Delta E(t; \lambda)$ explicitly dependent on $\lambda$, we obtain from Eq. (47)

$$(\partial/\partial\lambda)\ \mathrm{Re}\,\Delta E(t; \lambda) = \langle\Psi(\lambda)|\, H^{(1)} \,|\Psi(\lambda)\rangle - i\hbar(\partial/\partial t)\langle\chi(\lambda)|\, \partial\chi(\lambda)/\partial\lambda\rangle. \quad (48)$$

We recognize the first term on the right-hand side of Eq. (48) as the expectation value of the perturbation Hamiltonian, which provides the physical "response" of the system.[41] In the case of a system with a periodic Hamiltonian, it is appropriate to introduce a time average over one period in order to isolate the mean energy level shift $\Delta E(\lambda)$ in the phase factor $\mathrm{Re}\,\Delta E(t; \lambda)$;

$$\Delta E(\lambda) = \{\mathrm{Re}\,\Delta E(t; \lambda)\} \equiv (1/\tau)\int_t^{t+\tau} \mathrm{Re}\,\Delta E(t'; \lambda)\, dt'. \quad (49)$$

Employing such a time average over Eq. (48) gives

$$(\partial/\partial\lambda)\{\mathrm{Re}\,\Delta E(t; \lambda)\} = \{\langle\Psi(\lambda)|\, H^{(1)} \,|\Psi(\lambda)\rangle\} \quad (50)$$

since the time average over one period of the second term on the right-hand side of Eq. (48) vanishes. Consequently, from Eqs. (49) and (50), we have

$$\Delta E = \{\mathrm{Re}\,\Delta E(t)\} = \int_0^1 \{\langle\Psi(\lambda)|\, H^{(1)} \,|\Psi(\lambda)\rangle\}\, d\lambda, \quad (51)$$

and have identified the energy level shift appearing in Eq. (45) as equal to the time average of the system response, integrated over the strength of the perturbation. The quantity $\Delta E$ corresponds to the energy of induction associated with the application of an oscillatory perturbation to the system and provides the physically significant level shift.[42]

It is important to recognize that the expressions given for $\Psi(\mathbf{r}, t)$ in Eqs. (33) and (40) have been obtained from the general ansatz [Eq. (21)] as a consequence only of the Schrödinger equation [Eq. (1)] and the initial conditions [Eqs. (3)]. We do not introduce either Eq. (33) or (40) as an ansatz, but rather derive their forms from the Schrödinger equation and the assumed Hermiticity of the total Hamiltonian.[43] It is clear that the regular function $\phi(\mathbf{r}, t)$ satisfying Eq. (28b) and the intermediate normalization convention [Eq. (23)] is the essential part of the wave function. That is, $a_0(t)$, which furnishes a time-dependent phase in the wave function and the system level shift, as well as the normalization factor, is determined by Eq. (29), and the complete wave function is consequently determined by Eqs. (21) and (33).

In certain instances it is possible to obtain an exact solution of Eq. (1) for the total wave function $\Psi(\mathbf{r}, t)$ by determining closed form expressions for the $a_k(t)$ of Eq. (9). The factoring of the wave function we have introduced in Eqs. (20)–(33) will then be apparent, and explicit expressions for the $b_k(t)$ [Eq. (20b)] are obtained. No particular advantage results from solving Eqs. (28) rather than Eqs. (1) or (10) in such cases, and it is important to recognize that both approaches result in the same wave function, emphasizing that the development of Eqs. (20)–(33) merely provides a convenient rearrangement of the Dirac variation-of-constants solution.[36] In most applications, however, exact solution of the Schrodinger equation is not possible and we are interested in perturbative approximations to the wave function. The development of Eqs. (20)–(33) is more convenient in this case than is the original Dirac approach [Eqs. (9)–(19)] upon which it is based. This is because the wave function of Eq. (33) provides concise expressions for the normalization and phase factors, whereas in the Dirac approach they appear in expanded form. It remains only to determine a perturbation solution for the regular function $\phi(\mathbf{r}, t)$ of Eqs. (28), from which the associated perturbation approximations to $\chi(\mathbf{r}, t)$ and $\Psi(\mathbf{r}, t)$ are then obtained.

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[40] See, for example, Hayes and Parr (1961), and references cited therein.

[41] In the case of a nonresonant electromagnetic perturbation applied to a molecular system, the expectation value of the perturbation gives the induced electric and magnetic moments, which contain the various electromagnetic susceptibilities. These susceptibilities describe the physical response of the system to the applied perturbation. A general discussion of response theory is given by Peterson (1967).

[42] In the case of a nonresonant electromagnetic perturbation in the uniform-electric-field approximation, the right-hand side of Eq. (51) corresponds to the energy of induction associated with the application of the external oscillatory electric field. In essence, the nonzero mean-square electric field performs a finite amount of work on the polarization vector during the course of its induction, identifying $\Delta E$ in this case as the ac Stark shift. For a simplified discussion of this level shift see, for example, Pancharatham (1966).

[43] A wave function in the form of Eqs. (33), (40), and (45) also arises in connection with transition phenomena, which are somewhat outside our range of interests here. It is implicit, for example, in the lineshape and level-shift theories of Dirac (1927c) and Weisskopf and Wigner (1930) and in the more recent work of Lin and Bersohn (1966). Moreover, the form of Eqs. (33) and (40) is essential for obtaining the correct long-time behavior of the wave function in the transition case. In this connection, see the closely related work of Brooks and Scarfone (1969), who employ the multiple-time-scales formalism we discuss in Sec. IV.B for the dispersion case, or the more recent related discussion of Salzman (1971, 1972). Absorption and dispersion profiles in the neighborhood of resonances can also be approximated by employing $S$-matrix theory, as discussed, for example, by Shore (1967). Nevertheless, the particular form of Eqs. (33) and (40) is implicit in such developments, as well. Wave functions for magnetic resonance problems of the Rabi or Bloch–Siebert type are also similar to Eqs. (33) and (40) in that the secular terms which arise from a level shift are incorporated into an overall phase factor by introducing a transformation to a rotating frame of reference. See, for example, Slichter (1963) p. 26.

### C. Perturbation Theory

To solve Eqs. (28), we introduce the perturbation expansions

$$\phi(\mathbf{r},t)=\sum_{n=0}^{\infty}\phi^{(n)}(\mathbf{r},t), \tag{52a}$$

$$\Delta E(t)=\sum_{n=1}^{\infty}E^{(n)}(t), \tag{52b}$$

which results in the sequence of equations

$$[H^{(0)}(\mathbf{r})-E_0^{(0)}-i\hbar(\partial/\partial t)]\phi^{(1)}(\mathbf{r},t)+[H^{(1)}(\mathbf{r},t)-E^{(1)}(t)]\phi_0^{(0)}(\mathbf{r})=0, \tag{53a}$$

$$[H^{(0)}(\mathbf{r})-E_0^{(0)}-i\hbar(\partial/\partial t)]\phi^{(n)}(\mathbf{r},t)+[H^{(1)}(\mathbf{r},t)-E^{(1)}(t)]\phi^{(n-1)}(\mathbf{r},t)=\sum_{k=2}^{n}E^{(k)}(t)\phi^{(n-k)}(\mathbf{r},t), \quad n>1, \tag{53b}$$

with the conditions [Eq. (23)]

$$\langle\phi_0^{(0)}\mid\phi^{(n)}\rangle=0 \qquad n>0. \tag{53c}$$

The complex quantity $E^{(n)}(t)$ is given by

$$E^{(n)}(t)=\langle\phi_0^{(0)}\mid H^{(1)}\mid\phi^{(n-1)}\rangle \qquad n>0, \tag{53d}$$

which insures that the linear inhomogeneous perturbation equations [Eqs. (53a) and (53b)] possess nontrivial particular solutions.[44] Equations (53) correspond in form to the equations of time-independent perturbation theory in the intermediate normalization convention[34] and are suitable for solution by a variety of procedures. In subsequent sections we shall discuss specific applications of Eqs. (53) to particular perturbations.

It is instructive to consider in detail the alternative function $\chi(\mathbf{r},t)$ [Eq. (36)] and its perturbation approximation, which incorporates the normalization factor of Eq. (33) but not the secular terms. Introducing the perturbation expansions

$$\chi(\mathbf{r},t)=\sum_{n=0}^{\infty}\lambda^n\chi^{(n)}(\mathbf{r},t), \tag{54}$$

$$\langle\phi\mid\phi\rangle=1+\sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\lambda^{n+m}\langle\phi^{(n)}\mid\phi^{(m)}\rangle, \tag{55}$$

and that of Eq. (52a), into Eq. (36), where the perturbation parameter $\lambda$ is employed for convenience, we obtain explicit expressions for the $\chi^{(n)}(\mathbf{r},t)$,

$$\chi^{(0)}(\mathbf{r})=\phi_0^{(0)}(\mathbf{r}), \tag{56a}$$

$$\chi^{(1)}(\mathbf{r},t)=\phi^{(1)}(\mathbf{r},t), \tag{56b}$$

$$\chi^{(2)}(\mathbf{r},t)=\phi^{(2)}(\mathbf{r},t)-\tfrac{1}{2}\langle\phi^{(1)}\mid\phi^{(1)}\rangle\phi_0^{(0)}(\mathbf{r}), \tag{56c}$$

$$\chi^{(3)}(\mathbf{r},t)=\phi^{(3)}(\mathbf{r},t)-\tfrac{1}{2}\langle\phi^{(1)}\mid\phi^{(1)}\rangle\phi^{(1)}(\mathbf{r},t)-\tfrac{1}{2}(\langle\phi^{(2)}\mid\phi^{(1)}\rangle+\langle\phi^{(1)}\mid\phi^{(2)}\rangle)\phi_0^{(0)}(\mathbf{r}), \tag{56d}$$

$$\chi^{(n)}(\mathbf{r},t)=\sum_{l=0}^{n}(1/l!)[(\partial^l/\partial\lambda^l)\langle\phi\mid\phi\rangle^{-1/2}]_{\lambda=0}\phi^{(n-l)}(\mathbf{r},t). \tag{56e}$$

[44] This is by no means self-evident from Eqs. (53) and must be demonstrated explicitly for each specific perturbation. We do so for the harmonic perturbation considered in Sec. III.C.

The $\chi^{(n)}(\mathbf{r},t)$ of Eqs. (56) satisfy differential equations which are obtained most directly by substituting Eq. (54) into Eqs. (41). There results the sequence of equations

$$[H^{(0)}(\mathbf{r})-E_0^{(0)}-i\hbar(\partial/\partial t)]\chi^{(1)}(\mathbf{r},t)+[H^{(1)}(\mathbf{r},t)-E_R^{(1)}(t)]\chi^{(0)}(\mathbf{r})=0,$$

$$E_R^{(1)}(t)=\langle\chi^{(0)}\mid H^{(1)}\mid\chi^{(0)}\rangle-i\hbar\langle\chi^{(0)}\mid\partial\chi^{(1)}/\partial t\rangle, \tag{57a}$$

$$[H^{(0)}(\mathbf{r})-E_0^{(0)}-i\hbar(\partial/\partial t)]\chi^{(n)}(\mathbf{r},t)+[H^{(1)}(\mathbf{r},t)-E_R^{(1)}(t)]\chi^{(n-1)}(\mathbf{r},t)=\sum_{k=2}^{n}E_R^{(k)}(t)\chi^{(n-k)}(\mathbf{r},t), \quad n>1, \tag{57b}$$

with

$$E_R^{(n)}(t)=\langle\chi^{(0)}\mid H^{(1)}-E_R^{(1)}\mid\chi^{(n-1)}\rangle-\sum_{k=2}^{n-1}E_R^{(k)}(t)\langle\chi^{(0)}\mid\chi^{(n-k)}\rangle-i\hbar\langle\chi^{(0)}\mid\partial\chi^{(n)}/\partial t\rangle \qquad n>1, \tag{57c}$$

and

$$\sum_{k=0}^{n}\langle\chi^{(k)}\mid\chi^{(n-k)}\rangle=0 \qquad n>0. \tag{57d}$$

We recognize that Eqs. (57) are similar in form to the equations of time-independent perturbation theory employing the normalization convention of Eq. (37). The functions $\chi^{(n)}(\mathbf{r},t)$ are not uniquely specified by Eqs. (57); that is, they are arbitrary with respect to the addition of imaginary time-independent multiples of $\chi^{(0)}(\mathbf{r})$, since the normalization conditions [Eq. (57d)] specify only the real parts of such multiples. If these imaginary multiples are set equal to zero, in correspondence with the standard phase convention of time-independent perturbation theory,[45] the solutions of Eqs. (57) are identical with the functions $\chi^{(n)}(\mathbf{r},t)$ of Eqs. (56). Moreover, in this case, the $E_R^{(n)}(t)$ of Eq. (57c) are equal to the $\mathrm{Re}\,E^{(n)}(t)$ of Eqs. (35) and (53d);

$$E_R^{(n)}(t)=\mathrm{Re}\,E^{(n)}(t)=\mathrm{Re}\,\langle\phi^{(0)}\mid H^{(1)}\mid\phi^{(n-1)}\rangle. \tag{57e}$$

If this phase convention is not adopted,[46] the additional (arbitrary) terms that appear in the functions $\chi^{(n)}(\mathbf{r},t)$

[45] See, for example, Condon and Shortley (1963) pp. 30–34, and Epstein (1968c), for discussions of this aspect of time-independent perturbation theory.

[46] The importance of adopting the standard phase convention in the solution of Eqs. (57) has been somewhat misunderstood in the literature. Equations (57) have been previously obtained by Chung (1967), who apparently did not recognize the indeterminancy in their solutions and obtained incorrect results in their application to the Hartree–Fock approximation (see Sec. III.E). This feature of Chung's development has been noted by Heinrichs (1968a), who also derived Eqs. (57). Heinrichs makes the proper phase choice, on the basis of convenience, and therefore obtains correct results in his applications. However, the reason for employing the standard phase choice of time-independent perturbation theory is made completely clear only by identifying the function $\phi(\mathbf{r},t)$ and its relations to $\Psi(\mathbf{r},t)$ through the development of Eqs. (20)–(51). Perturbation approaches based on Eqs. (57) have also been discussed previously by Van Hove (1955a, b) and Ezawa (1963) p. 93.

can be incorporated into an over-all phase factor as in the static case and, consequently, the solution differs from that of Eqs. (36) and (56) only by this over-all time-independent phase factor.[45] The $E_R^{(n)}(t)$ of Eq. (57c) are, in this case, not equal to the $\mathrm{Re}\,E^{(n)}(t)$ of Eq. (57e). Consequently, in order for the solutions of Eqs. (57) to be equivalent to the Dirac variation-of-constants results and to those of Eqs. (56), it is necessary to enforce the customary phase convention of time-independent perturbation theory. By contrast, in solving Eqs. (53) it is necessary to insure that the simpler orthogonality condition of Eq. (53c) is satisfied. Thus, Eqs. (53) are somewhat more suitable for computational application than Eqs. (57) because of the inclusion in the latter of the redundant normalization terms.

Having introduced the additional perturbation functions $\chi^{(n)}(\mathbf{r}, t)$, which incorporate the normalization but not the secular terms, we next consider the complete time-dependent perturbation functions $\Psi^{(n)}(\mathbf{r}, t)$ of Eqs. (19). From Eq. (40), by expanding the exponential factor, we obtain

$$\Psi^{(0)}(\mathbf{r}, t)=\chi^{(0)}(\mathbf{r})\,\exp\left[(i\hbar)^{-1}E_0^{(0)}t\right], \tag{58a}$$

$$\Psi^{(1)}(\mathbf{r}, t)=\left[\chi^{(1)}(\mathbf{r}, t)+(i\hbar)^{-1}\int_{-\infty}^{t}\mathrm{Re}\,E^{(1)}(t')\,dt'\chi^{(0)}(\mathbf{r})\right]\exp\left[(i\hbar)^{-1}E_0^{(0)}t\right], \tag{58b}$$

$$\begin{aligned}\Psi^{(2)}(\mathbf{r}, t)=\Bigg[&\chi^{(2)}(\mathbf{r}, t)+(i\hbar)^{-1}\int_{-\infty}^{t}\mathrm{Re}\,E^{(1)}(t')\,dt'\chi^{(1)}(\mathbf{r}, t)+(i\hbar)^{-1}\int_{-\infty}^{t}\mathrm{Re}\,E^{(2)}(t')\,dt'\chi^{(0)}(\mathbf{r})\\&+\tfrac{1}{2}(i\hbar)^{-2}\left(\int_{-\infty}^{t}\mathrm{Re}\,E^{(1)}(t')\,dt'\right)^2\chi^{(0)}(\mathbf{r})\Bigg]\exp\left[(i\hbar)^{-1}E_0^{(0)}t\right],\end{aligned} \tag{58c}$$

$$\begin{aligned}\Psi^{(3)}(\mathbf{r}, t)=\Bigg[&\chi^{(3)}(\mathbf{r}, t)+(i\hbar)^{-1}\int_{-\infty}^{t}\mathrm{Re}\,E^{(1)}(t')\,dt'\chi^{(2)}(\mathbf{r}, t)+(i\hbar)^{-1}\int_{-\infty}^{t}\mathrm{Re}\,E^{(2)}(t')\,dt'\chi^{(1)}(\mathbf{r}, t)\\&+(i\hbar)^{-1}\int_{-\infty}^{t}\mathrm{Re}\,E^{(3)}(t')\,dt'\chi^{(0)}(\mathbf{r})+\tfrac{1}{2}(i\hbar)^{-2}\left(\int_{-\infty}^{t}\mathrm{Re}\,E^{(1)}(t')\,dt'\right)^2\chi^{(1)}(\mathbf{r}, t)\\&+(i\hbar)^{-2}\left(\int_{-\infty}^{t}\mathrm{Re}\,E^{(1)}(t')\,dt'\right)\left(\int_{-\infty}^{t}\mathrm{Re}\,E^{(2)}(t')\,dt'\right)\chi^{(0)}(\mathbf{r})+\tfrac{1}{6}(i\hbar)^{-3}\left(\int_{-\infty}^{t}\mathrm{Re}\,E^{(1)}(t')\,dt'\right)^3\chi^{(0)}(\mathbf{r})\Bigg]\exp\left[(i\hbar)^{-1}E_0^{(0)}t\right],\end{aligned} \tag{58d}$$

$$\Psi^{(n)}(\mathbf{r}, t)=\sum_{l=0}^{n}(l!)^{-1}\left[\frac{\partial^l}{\partial\lambda^l}\exp\left((i\hbar)^{-1}\int_{-\infty}^{t}\mathrm{Re}\,\Delta E(t')\,dt'\right)\right]_{\lambda=0}\chi^{(n-l)}(\mathbf{r}, t)\,\exp\left[(i\hbar)^{-1}E_0^{(0)}t\right], \tag{58e}$$

where the perturbation parameter $\lambda$ in Eq. (58e) is introduced for convenience, as in Eq. (56e). That the functions given by Eqs. (58) are the correct perturbation solutions of the Schrödinger equation can be seen by substituting them into Eqs. (19), resulting in the perturbation sequence of Eqs. (57) satisfied by the $\chi^{(n)}(\mathbf{r}, t)$. The functions $\Psi^{(n)}(\mathbf{r}, t)$ expressed in terms of the $\chi^{(n)}(\mathbf{r}, t)$ show explicitly the presence of secular terms which do not contribute to the expectation values of Hermitian operators. Of the terms appearing in Eqs. (58) for order $n$, only the first one, $\chi^{(n)}(\mathbf{r}, t)$, contributes to an expectation value. The others, which arise from the expansion of the phase factor of Eq. (40), yield contributions which cancel identically in each order of the perturbation expansion.[33] Further, it is evident that the time integrals in Eqs. (58) do not necessarily result in simple linear, quadratic, etc., time dependences (secular divergence) but, rather, can give rise to more general secular behavior. The customary Dirac variation-of-constants solutions, Eqs. (9)–(19), can also be "rearranged" into the form of Eqs. (58), although it is somewhat complicated to "uncover" the secular terms following such a procedure.[32] By contrast, the development of Eqs. (20)–(40) performs the extraction of both secular and normalization terms in a direct and concise manner.

To relate the $\Psi^{(n)}(\mathbf{r}, t)$ to the basic functions $\phi^{(n)}(\mathbf{r}, t)$, it is possible to simply introduce the expressions for $\chi^{(n)}(\mathbf{r}, t)$ in terms of the $\phi^{(n)}(\mathbf{r}, t)$ [Eqs. (56)]. It is also instructive, however, to see explicitly how the normalization terms arise in the perturbation functions $\Psi^{(n)}(\mathbf{r}, t)$ from expansion of the factor $a_0(t)$. To demonstrate this, we

return to Eqs. (21) and (29) and expand the complete complex exponential factor, $a_0(t)$, to obtain

$$\Psi^{(0)}(\mathbf{r},t)=\phi_0^{(0)}(\mathbf{r})\exp\left[(i\hbar)^{-1}E_0^{(0)}t\right], \tag{59a}$$

$$\Psi^{(1)}(\mathbf{r},t)=\left[\phi^{(1)}(\mathbf{r},t)+(i\hbar)^{-1}\int_{-\infty}^{t}E^{(1)}(t')\,dt'\phi_0^{(0)}(\mathbf{r})\right]\exp\left[(i\hbar)^{-1}E_0^{(0)}t\right], \tag{59b}$$

$$\Psi^{(2)}(\mathbf{r},t)=\left[\phi^{(2)}(\mathbf{r},t)+(i\hbar)^{-1}\int_{-\infty}^{t}E^{(1)}(t')\,dt'\phi^{(1)}(\mathbf{r},t)+(i\hbar)^{-1}\int_{-\infty}^{t}E^{(2)}(t')\,dt'\phi_0^{(0)}(\mathbf{r})\right.$$
$$\left.+\tfrac{1}{2}(i\hbar)^{-2}\left(\int_{-\infty}^{t}E^{(1)}(t')\,dt'\right)^2\phi_0^{(0)}(\mathbf{r})\right]\exp\left[(i\hbar)^{-1}E_0^{(0)}t\right], \tag{59c}$$

$$\Psi^{(3)}(\mathbf{r},t)=\left[\phi^{(3)}(\mathbf{r},t)+(i\hbar)^{-1}\int_{-\infty}^{t}E'^{(1)}(t')\,dt'\phi^{(2)}(\mathbf{r},t)+(i\hbar)^{-1}\int_{-\infty}^{t}E^{(2)}(t')\,dt'\phi^{(1)}(\mathbf{r},t)\right.$$
$$+(i\hbar)^{-1}\int_{-\infty}^{t}E^{(3)}(t')\,dt'\phi_0^{(0)}(\mathbf{r})+\tfrac{1}{2}(i\hbar)^{-2}\left(\int_{-\infty}^{t}E^{(1)}(t')\,dt'\right)^2\phi^{(1)}(\mathbf{r},t)$$
$$\left.+(i\hbar)^{-2}\left(\int_{-\infty}^{t}E^{(1)}(t')\,dt'\right)\left(\int_{-\infty}^{t}E^{(2)}(t')\,dt'\right)\phi_0^{(0)}(\mathbf{r})+\tfrac{1}{6}(i\hbar)^{-3}\left(\int_{-\infty}^{t}E^{(1)}(t')\,dt'\right)^3\phi_0^{(0)}(\mathbf{r})\right]\exp\left[(i\hbar)^{-1}E_0^{(0)}t\right], \tag{59d}$$

$$\Psi^{(n)}(\mathbf{r},t)=\sum_{l=0}^{n}(l!)^{-1}\left[(\partial^l/\partial\lambda^l)a_0(t)\right]_{\lambda=0}\phi^{(n-l)}(\mathbf{r},t)\exp\left[(i\hbar)^{-1}E_0^{(0)}t\right], \tag{59e}$$

once again introducing the parameter $\lambda$ for convenience. To make clear which of the terms in Eqs. (59) provide for the proper normalization, the integrals appearing there are written

$$\int_{-\infty}^{t}E^{(n)}(t')\,dt'=\int_{-\infty}^{t}\mathrm{Re}\,E^{(n)}(t')\,dt'+i\int_{-\infty}^{t}\mathrm{Im}\,E^{(n)}(t')\,dt', \tag{60}$$

where the Re $E^{(n)}(t)$ are given by Eq. (57e). To evaluate the terms involving Im $E^{(n)}(t)$, which in fact provide the proper normalization, we make use of the perturbation expansion of Eq. (30) and obtain [Im $E^{(1)}(t)=0$]

$$\hbar^{-1}\int_{-\infty}^{t}\mathrm{Im}\,E^{(2)}(t')\,dt'=-\tfrac{1}{2}\langle\phi^{(1)}\mid\phi^{(1)}\rangle, \tag{61a}$$

$$\hbar^{-1}\int_{-\infty}^{t}\mathrm{Im}\,E^{(3)}(t')\,dt'=-\tfrac{1}{2}(\langle\phi^{(1)}\mid\phi^{(2)}\rangle+\langle\phi^{(2)}\mid\phi^{(1)}\rangle), \tag{61b}$$

$$\hbar^{-1}\int_{-\infty}^{t}\mathrm{Im}\,E^{(4)}(t')\,dt'=-\tfrac{1}{2}(\langle\phi^{(3)}\mid\phi^{(1)}\rangle+\langle\phi^{(2)}\mid\phi^{(2)}\rangle+\langle\phi^{(1)}\mid\phi^{(3)}\rangle)-\hbar^{-1}\int_{-\infty}^{t}\langle\phi^{(1)}\mid\phi^{(1)}\rangle\,\mathrm{Im}\,E^{(2)}(t')\,dt', \tag{61c}$$

$$\hbar^{-1}\int_{-\infty}^{t}\mathrm{Im}\,E^{(n)}(t')\,dt'=-\tfrac{1}{2}\sum_{m=1}^{n-1}\langle\phi^{(m)}\mid\phi^{(n-m)}\rangle-\hbar^{-1}\sum_{k=2}^{n-2}\sum_{m=1}^{n-k-1}\int_{-\infty}^{t}\langle\phi^{(m)}\mid\phi^{(n-k-m)}\rangle\,\mathrm{Im}\,E^{(k)}(t')\,dt' \qquad n\geq 4. \tag{61d}$$

Inserting these expressions into Eqs. (59), we rederive Eqs. (58) but with the $\chi^{(n)}(\mathbf{r},t)$ replaced by their expansions in terms of the $\phi^{(n)}(\mathbf{r},t)$ [Eqs. (56)]. This procedure avoids explicit expansion of the normalization factor [Eqs. (54)–(56)] and makes direct use of the perturbation expansion of Eq. (30). Of course, the two methods give identical results for the total time-dependent functions and their convergence properties are equivalent.

The perturbation functions $\Psi^{(n)}(\mathbf{r},t)$ given in Eqs. (58) and (59) show how both the normalization and secular terms are introduced explicitly by expansion of the multiplicative time-dependent factor of Eq. (32). Since the customary perturbation theory treatment based on the Dirac variation-of-constants method results in the expanded form of the normalization and phase factor, it is clear that the conventional perturbation approach [Eqs. (9)–(19)] gives rise to the secular and normalization terms appearing in Eqs. (58) and (59). It is important to emphasize, however, that the expectation values of physical properties obtained with the Dirac solution of Eqs. (9)–(19) or with solutions in the form of Eqs. (33) and (52), or (40) and (54) are the same. That is, from Eqs. (33) and (40) we have

$$\langle\Psi\mid A\mid\Psi\rangle=\langle\chi\mid A\mid\chi\rangle=\langle\phi\mid A\mid\phi\rangle\langle\phi\mid\phi\rangle^{-1}, \tag{62}$$

for $A$ an Hermitian operator representing a physical observable.[33] Since the secular terms do not appear in

Eq. (62) or its perturbation expansion, they cannot introduce difficulties, and it is thus erroneous to conclude that Eq. (13) or the expansion of Eq. (62) is invalid due to their presence. On the other hand, the *rapidity* of convergence of the expansion of Eq. (62) is a separate matter which depends upon the nature of the perturbation and is not considered here.

Our introduction of the $\phi^{(n)}(\mathbf{r}, t)$ is motivated primarily by the fact that they provide a convenient means for exhibiting the normalization and secular terms in the perturbation expansion of the complete wave function. They also provide for the formulation of a set of equations suitable for computational purposes and for clarifying the behavior of the time-dependent perturbation equations in the static limit. The distinct advantages of the equations satisfied by the $\phi^{(n)}(\mathbf{r}, t)$ over those for the $\Psi^{(n)}(\mathbf{r}, t)$ and $\chi^{(n)}(\mathbf{r}, t)$ will be further clarified by the applications given in the following section (Sec. III) and in our subsequent discussion of variational procedures (Sec. V).

## III. APPLICATIONS

To illustrate the general formulation of the previous section, it is instructive to make comparisons among the three sets of perturbation functions, $\phi^{(n)}(\mathbf{r}, t)$, $\chi^{(n)}(\mathbf{r}, t)$, and $\Psi^{(n)}(\mathbf{r}, t)$, obtained for specific perturbation problems. We consider first the model problem of a one-dimensional harmonic oscillator perturbed by a potential for which the Schrödinger equation can be solved exactly. We then treat general static and harmonic perturbations, and apply the latter development to the determination of the nonlinear dipole polarization of a molecule by an oscillating uniform electric field. The form of the uncoupled Hartree–Fock equations in the presence of a general one-particle time-dependent perturbation is then derived to illustrate the importance of extracting secular and normalization terms from the wave function prior to computational applications.

### A. The Linearly Perturbed Oscillator

The one-dimensional harmonic oscillator perturbed by an arbitrary time-dependent potential linear in the oscillator coordinate provides an instructive example of the factoring of the secular and normalization terms from the wave function described in Eqs. (20)–(33). The unperturbed Hamiltonian

$$H^{(0)}(z) = -(\hbar^2/2m)(\partial^2/\partial z^2) + \tfrac{1}{2}Kz^2, \quad (63a)$$

appearing in the time-independent Schrödinger equation

$$[H^{(0)}(z) - E_k^{(0)}]\phi_k^{(0)}(z) = 0, \qquad k = 0, 1, 2, \cdots \quad (63b)$$

gives rise to the well-known spectrum $[E_k^{(0)}, \phi_k^{(0)}(z)]$, where

$$E_k^{(0)} = (k + \tfrac{1}{2})\hbar\omega_0, \qquad \omega_0 = (K/m)^{1/2}, \quad (63c)$$

and the $\phi_k^{(0)}(z)$ are the familiar harmonic oscillator eigenfunctions.[47] The perturbation we consider is written in the form

$$H^{(1)}(z, t) = zg(t) \quad (64)$$

where the function $g(t)$ is arbitrary, within the conditions on $H^{(1)}(z, t)$ specified in Sec. II. Exact solution of Eq. (1) is obtained in this case,[48] providing explicit expressions for the $a_k(t)$ of Eq. (9) in the form

$$a_k(t) = a_0(t)\,(k!)^{-1/2}[iX(t)]^k, \quad (65)$$

where

$$X(t) = -(2m\hbar\omega_0)^{-1/2}\int_{-\infty}^{t} \exp[i\omega_0 t']g(t')\,dt', \quad (66)$$

and $a_0(t)$ is given by [Eq. (29)]

$$a_0(t) = \exp\left((i\hbar)^{-1}\int_{-\infty}^{t}\Delta E(t')\,dt'\right)$$

$$= \exp\left[(2m\hbar\omega_0)^{-1/2} \times \int_{-\infty}^{t}\exp[-i\omega_0 t']g(t')X(t')\,dt'\right]. \quad (67)$$

The factoring we have introduced in Eq. (20) is explicitly illustrated by Eq. (65) and we identify, for the perturbation of Eq. (64),

$$b_k(t) = (k!)^{-1/2}[iX(t)]^k. \quad (68)$$

To demonstrate the normalization of the wave function [Eq. (31)], we consider $\mathrm{Im}\,\Delta E(t)$ in Eq. (67) and find, from Eqs. (22), (28c), and (68), that

$$\exp\left[(\hbar)^{-1}\int_{-\infty}^{t}\mathrm{Im}\,\Delta E(t')\,dt'\right] = \exp[-\tfrac{1}{2}|X(t)|^2], \quad (69)$$

and

$$\langle\phi|\phi\rangle = \sum_{k=0}^{\infty}(k!)^{-1}(|X(t)|^2)^k = \exp[|X(t)|^2]. \quad (70)$$

Equations (69) and (70) provide an explicit example of how the correct normalization of the wave function is insured by an over-all multiplicative factor [Eq. (31)]. Finally, $\mathrm{Re}\,\Delta E(t)$, which incorporates the system level shift, can be evaluated from Eqs. (66) and (67) for specific perturbations $g(t)$.

As a preliminary to the general static and harmonic perturbations considered below (Secs. III.B and III.C), we examine here the harmonic perturbation

$$g(t) = f(t)\cos\omega t, \quad (71)$$

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[47] See, for example, Pauling and Wilson (1935) p. 65, who provide a particularly detailed discussion of the quantum mechanical harmonic oscillator.

[48] See, for example, Feynman (1948), Husimi (1953), Kerner (1958), and Pechukas and Light (1966).

where $f(t)$ is an appropriate switching function.[49] In the case of ideal adiabatic switching, we find [Eq. (66)], for $t\rightarrow+\infty$,

$$X(t)=(\tfrac{1}{2}i)(2m\hbar\omega_0)^{-1/2}\times\left\{\frac{\exp[i(\omega_0+\omega)t]}{(\omega_0+\omega)}+\frac{\exp[i(\omega_0-\omega)t]}{(\omega_0-\omega)}\right\},\quad(72)$$

and [Eq. (67)]

$$a_0(t)=\exp\left\{-(1/4)(2m\hbar\omega_0)^{-1}\times\left[\tfrac{1}{2}(\omega_0+\omega)^{-2}+\tfrac{1}{2}(\omega_0-\omega)^{-2}+\frac{\cos 2\omega t}{(\omega_0^2-\omega^2)}-\frac{i2\omega_0}{(\omega_0^2-\omega^2)}\left(t+\frac{\sin 2\omega t}{2\omega}\right)\right]\right\},\quad(73)$$

with the $a_k(t)$ given by Eq. (65). When expressed in the form of Eq. (33), the over-all wave function is seen to be highly compact, whereas the customary perturbation functions $\Psi^{(n)}(z,t)$ [Eqs. (59)] contain the secular and normalization terms which arise from expansion of Eq. (73). We note that both diverging and oscillatory secular terms arise from the expansion of the phase factor.[50]

In the static limit, $\omega\rightarrow0$, Eqs. (72) and (73) become

$$X(t)=(i/\omega_0)(2m\hbar\omega_0)^{-1/2}\exp(i\omega_0 t)\quad(74)$$

$$a_0(t)=\exp\{-(1/2)(2m\hbar\omega_0)^{-1}[1/\omega_0^2-i(2/\omega_0)t]\}.\quad(75)$$

The wave function and level shift given by Eqs. (74) and (75) are in agreement with the results obtained from the time-independent Schrödinger equation and are, therefore, consistent with the adiabatic theorem.[35] It is important to note that the oscillatory part of the phase factor in Eq. (73) contributes to the static level shift [Eq. (75)] in the limit $\omega\rightarrow0$. Consequently, in order to insure uniform passage to the static limit, it is necessary in the time-dependent case to extract into a phase factor not just secular divergent terms, but also secular terms which become divergent in the static limit. The development of Eqs. (20)–(33) performs the extraction of both secular and normalization terms concisely and the specific example considered here provides an explicit illustration of the procedure.

### B. Static Perturbations

In the case of an adiabatically switched-on static perturbation (we use the subscript $s$ to designate the static case)

$$H^{(1)}(\mathbf{r},t)=H_s^{(1)}(\mathbf{r})f(t),\quad(76)$$

the adiabatic theorem assures that for $t\rightarrow+\infty$ the solution given in Eqs. (33) and (40) takes the form

$$\Psi_s(\mathbf{r},t)=\phi_s(\mathbf{r})\langle\phi_s\mid\phi_s\rangle^{-1/2}\exp[(i\hbar)^{-1}(E_0^{(0)}+\Delta E_s)t]=\chi_s(\mathbf{r})\exp[(i\hbar)^{-1}(E_0^{(0)}+\Delta E_s)t].\quad(77)$$

Here, $\Delta E_s$ is the static energy level shift [Eqs. (35) and (41b)]

$$\Delta E_s=\langle\phi_0^{(0)}\mid H_s^{(1)}\mid\phi_s\rangle=\langle\chi^{(0)}\mid H_s^{(1)}\mid\chi_s\rangle/\langle\chi^{(0)}\mid\chi_s\rangle=\langle\Psi^{(0)}\mid H_s^{(1)}\mid\Psi_s\rangle/\langle\Psi^{(0)}\mid\Psi_s\rangle.\quad(78a)$$

It is important to recognize that Eqs. (77) and (78a) are valid in the limit $t\rightarrow+\infty$, subsequent to the required ideal adiabatic switching interval. Within the switching interval, the wave function [Eq. (33)] and level shift [Eq. (35)] depend on the particular switching function employed. To emphasize the requirement of an infinite switching interval, we can write the level shift in the alternative form, based on Eq. (28e) and familar from "many-body" theory,[51]

$$\Delta E_s=\lim\,(t\rightarrow+\infty)[i\hbar(\partial/\partial t)\ln\langle\Psi^{(0)}\mid\Psi\rangle].\quad(78b)$$

In Eqs. (77) and (78), $\phi_s(\mathbf{r})$ and $\chi_s(\mathbf{r})$ are the static limits of $\phi(\mathbf{r},t)$ and $\chi(\mathbf{r},t)$, respectively. The functions $\phi_s(\mathbf{r})$ and $\chi_s(\mathbf{r})$ thus satisfy the time-independent forms of Eqs. (28) and (41), respectively, and the associated time-independent perturbation functions, $\phi_s^{(n)}(\mathbf{r})$ and $\chi_s^{(n)}(\mathbf{r})$, satisfy the static limits of Eqs. (53) and (57), respectively. We recognize that the distinction between the functions $\phi_s^{(n)}(\mathbf{r})$ and $\chi_s^{(n)}(\mathbf{r})$ is due to the difference in the normalization conventions [Eqs. (53c) and (57d)], both of which are used in time-independent perturbation theory.[34,45] In obtaining solutions of the time-independent form of Eqs. (57), it is also necessary to enforce the phase convention of sequentially neglecting arbitrary imaginary multiples of $\chi_s^{(0)}(\mathbf{r})$ in the functions $\chi_s^{(n)}(\mathbf{r})$, since they are not uniquely specified by the normalization requirement. This procedure insures

[49] A variety of switching functions can be employed, ranging from the sudden to the adiabatic forms. The simple piecewise function $f(t)=\exp[\delta t]$, $t\leq0$; $f(t)=1$, $t\geq0$, with $\delta$ real has a discontinuous first derivative, but is adequate for our purposes. Taking $\delta\gg\omega_0$, we obtain the case of sudden switching, while for $\delta\ll\omega_0$ we have the case of adiabatic switching. Employing this switching function, we find that $a_0(t)$ [Eq. (67)] for the harmonic perturbation of Eq. (71) contains a phase factor $\approx1/\delta$ which diverges in the adiabatic limit $\delta\rightarrow0$. This divergent factor can be avoided by employing a sufficiently smooth and continuous switching function, as discussed, for example, by Musher (1964). An alternative justification for deleting the divergent portion of the phase factor is that the "physical" level shift is given by Eq. (35), wherein the divergent phase cancels out. See, for example, Gell-Mann and Low (1951), for discussion of this point. In the following we assume the possibility of "ideal" adiabatic switching, for which the level shift is taken to be independent of the switching function by deleting the divergent phase.

[50] The wave function obtained from Eqs. (72) and (73) is an illustration of the quasiperiodic state discussed in Footnote 39. The level shift term in Eq. (73) evidently exhibits a frequency dependence similar to that of the dynamic polarizability of the system first described by Kramers and Heisenberg (1925).

[51] From Eq. (30) we see that $\mathrm{Im}\Delta E(t)\rightarrow0$ in the limit $t\rightarrow+\infty$, since $\phi(\mathbf{r},t)\rightarrow\phi_s(\mathbf{r})$. Consequently, the level shift of Eq. (78b) is real. For an alternative discussion of Eq. (78b) see, for example, Mattuck (1969) Appendix C.

that the correct phase factor [Eq. (77)] will result, whereas including arbitrary nonzero imaginary multiples of $\chi_s^{(0)}(\mathbf{r})$ in the $\chi_s^{(n)}(\mathbf{r})$ is equivalent to introducing an additional time-independent phase factor into the wave function.[45] In solving the time-independent form of Eqs. (53), by contrast, we need insure only that Eq. (53c) is satisfied, since the correct normalization terms and phase factor are automatically introduced by the form of Eq. (77).

While the functions $\phi^{(n)}(\mathbf{r}, t)$ and $\chi^{(n)}(\mathbf{r}, t)$ are time-independent in the static limit, such is not the case for the $\Psi^{(n)}(\mathbf{r}, t)$. The latter functions remain time-dependent; from Eqs. (58) or (59), they have the form $(t \to +\infty)$

$$\Psi_s^{(0)}(\mathbf{r}, t) = \chi_s^{(0)}(\mathbf{r}) \exp\left[(i\hbar)^{-1}E_0^{(0)}t\right], \tag{79a}$$

$$\Psi_s^{(1)}(\mathbf{r}, t) = \left[\chi_s^{(1)}(\mathbf{r}) + (i\hbar)^{-1}E_s^{(1)}t\chi_s^{(0)}(\mathbf{r})\right] \exp\left[(i\hbar)^{-1}E_0^{(0)}t\right], \tag{79b}$$

$$\Psi_s^{(2)}(\mathbf{r}, t) = \left[\chi_s^{(2)}(\mathbf{r}) + (i\hbar)^{-1}E_s^{(1)}t\chi_s^{(1)}(\mathbf{r}) + (i\hbar)^{-1}E_s^{(2)}t\chi_s^{(0)}(\mathbf{r}) + \tfrac{1}{2}(i\hbar)^{-2}(E_s^{(1)}t)^2\chi_s^{(0)}(\mathbf{r})\right] \exp\left[(i\hbar)^{-1}E_0^{(0)}t\right], \tag{79c}$$

$$\Psi_s^{(3)}(\mathbf{r}, t) = \left[\chi_s^{(3)}(\mathbf{r}) + (i\hbar)^{-1}E_s^{(1)}t\chi_s^{(2)}(\mathbf{r}) + (i\hbar)^{-1}E_s^{(2)}t\chi_s^{(1)}(\mathbf{r}) + (i\hbar)^{-1}E_s^{(3)}t\chi_s^{(0)}(\mathbf{r}) + \tfrac{1}{2}(i\hbar)^{-2}(E_s^{(1)}t)^2\chi_s^{(1)}(\mathbf{r}) + (i\hbar)^{-2}(E_s^{(1)}t)(E_s^{(2)}t)\chi_s^{(0)}(\mathbf{r}) + \tfrac{1}{6}(i\hbar)^{-3}(E_s^{(1)}t)^3\chi_s^{(0)}(\mathbf{r})\right] \exp\left[(i\hbar)^{-1}E_0^{(0)}t\right], \tag{79d}$$

$$\Psi_s^{(n)}(\mathbf{r}, t) = \sum_{l=0}^{n} (l!)^{-1}\{(\partial^l/\partial\lambda^l) \exp\left[(i\hbar)^{-1}\Delta E_s t\right]\}_{\lambda=0}\chi_s^{(n-l)}(\mathbf{r}) \exp\left[(i\hbar)^{-1}E_0^{(0)}t\right], \tag{79e}$$

with

$$\Delta E_s = \sum_{n=1}^{\infty} \lambda^n E_s^{(n)} \tag{79f}$$

in Eq. (79e).

It is evident from Eqs. (79) that the expansion of the exponential [Eq. (77)] gives rise to time-divergent terms (secular divergences) in the perturbation functions $\Psi_s^{(n)}(\mathbf{r}, t)$. Such terms do not lead to divergence in expectation values for physical observables, however, since the contributions from the secular terms cancel in each order of perturbation theory. Their presence in the perturbation functions $\Psi_s^{(n)}(\mathbf{r}, t)$ is necessary to insure that the $\chi_s^{(n)}(\mathbf{r})$, or the $\phi_s^{(n)}(\mathbf{r})$, satisfy the proper time-independent perturbation equations; i.e., substitution of Eqs. (79) into Eqs. (19) leads directly to the static limits of Eqs. (57). It is customary to bypass the $\Psi_s^{(n)}(\mathbf{r}, t)$ in the time-independent case by introducing Eq. (77) as an ansatz, which leads directly to the static limit of Eqs. (53) or (57). From the present development it is clear that the $\Psi_s^{(n)}(\mathbf{r}, t)$ of Eqs. (79) are the correct solutions $(t \to +\infty)$ of Eqs. (19) for a static perturbation introduced adiabatically.

Consideration of the static limit makes possible a connection with the better known formulations of time-independent perturbation theory. This clarifies the nature of the three different conventions [Eqs. (19), (53), and (57)] introduced above into time-dependent perturbation theory and reinforces the conclusion that all of the conventions must yield the correct answer if properly executed.

### C. Harmonic Perturbations

Since harmonic perturbations play a fundamental role in the semiclassical treatment of the interactions between radiation and matter, we here apply the general development to an adiabatically switched-on harmonic perturbation. Introducing the switching function $f(t)$ previously employed,[49] we write the harmonic perturbation in the form

$$H^{(1)}(\mathbf{r}, t) = h^{(1)}(\mathbf{r})[\exp(i\omega t) + \exp(-i\omega t)]f(t), \tag{80}$$

where the spatial portion of the perturbation, $h^{(1)}(\mathbf{r})$, which is considered real for simplicity, is not specified at this point.

In the switching interval the complete wave function and the solutions of Eqs. (53) for the adiabatically applied harmonic perturbation [Eq. (80)] depend upon the specific choice of switching function. However, for $t \to +\infty$, when the steady state has been established, the solutions $\phi^{(n)}(\mathbf{r}, t)$ can be made independent of $f(t)$ by employing a sufficiently smooth (ideal) function. Further, since all of the secular terms have been collected in the phase factor of Eq. (33), the correct solutions of Eqs. (53) should be periodic in time,[39] similar to the result obtained for the perturbed harmonic oscillator in Sec. III.A [Eqs. (72) and (73)]. To clarify this, we write Eqs. (53a) and (53b) in the form

$$[H^{(0)}(\mathbf{r}) - E_0^{(0)} - i\hbar(\partial/\partial t)]\phi^{(n)}(\mathbf{r}, t) = \theta^{(n)}(\mathbf{r}, t) \qquad n \geq 1 \tag{81}$$

where $\theta^{(n)}(\mathbf{r}, t)$ is the inhomogeneous part of the equation, involving only known lower-order functions $\phi^{(k)}(\mathbf{r}, t)\,(k<n)$. The definition of $E^{(n)}(t)$ [Eq. (53d)] assures that

$$\langle\phi_0^{(0)} \mid \theta^{(n)}\rangle = 0, \tag{82}$$

and, consequently, from Eq. (81) we have

$$(\partial/\partial t)\langle\phi_0^{(0)} \mid \phi^{(n)}\rangle = 0, \qquad n \geq 1. \tag{83}$$

Since Eq. (83) is satisfied for all $t$, the initial conditions $\langle\phi_0^{(0)} \mid \phi^{(n)}\rangle \to 0$, $(t \to -\infty)$, $n \geq 1$, insure that the correct solutions of Eqs. (81) will satisfy the normalization

conditions of Eq. (53c). Thus, no multiples of the unperturbed eigenfunction $\phi_0^{(0)}(\mathbf{r})$ will appear in the correct solutions of Eqs. (81). Moreover, for $t\to+\infty$ the inhomogeneous terms $\theta^{(n)}(\mathbf{r},t)$ are seen from Eqs. (53) to be periodic functions of time for an harmonic perturbation, if the lower-order functions $\phi^{(k)}(\mathbf{r},t)(k<n)$ are periodic. The first-order function $\phi^{(1)}(\mathbf{r},t)$ is easily shown to be periodic and, consequently, all the $\theta^{(n)}(\mathbf{r},t)$ are periodic by induction. This, and the normalization condition of Eq. (53c), insures that the $\phi^{(n)}(\mathbf{r},t)$ of Eqs. (81) are periodic functions of the time.

Introduction of solutions of the form $(t\to+\infty)$

$$\phi^{(n)}(\mathbf{r},t)=\sum_k \phi_k^{(n)}(\mathbf{r})\exp(ik\omega t) \tag{84}$$

into Eq. (81) results in the equations

$$[H^{(0)}(\mathbf{r})-E_0^{(0)}+k\hbar\omega]\phi_k^{(n)}(\mathbf{r})=\theta_k^{(n)}(\mathbf{r}), \tag{85}$$

with [Eq. (82)]

$$\langle\phi_0^{(0)}\mid\theta_k^{(n)}\rangle=0, \tag{86}$$

where the contributing $k$ values and the functions $\theta_k^{(n)}(\mathbf{r})$ are determined order-by-order from the inhomogeneous terms $\theta^{(n)}(\mathbf{r},t)$. Equation (86) for $k\neq0$ insures that the $\phi_k^{(n)}(\mathbf{r})(k\neq0)$ are orthogonal to $\phi_0^{(0)}(\mathbf{r})$, while in the case $k=0$, Eq. (86) is the necessary and sufficient condition that nontrivial particular solutions $\phi_0^{(n)}(\mathbf{r})$ of Eq. (85) exist.[52] The nonuniqueness in the solution [i.e., the possibility of adding an arbitrary multiple of $\phi_0^{(0)}(\mathbf{r})$] is resolved by the requirement of our normalization condition that

$$\langle\phi_0^{(0)}\mid\phi_0^{(n)}\rangle=0 \qquad \text{[Eq. (53c)]}.[53]$$

For the harmonic perturbation, we find from Eq. (84) that the functions $\phi^{(n)}(\mathbf{r},t)$ through third order, subsequent to the switching interval, are

$$\phi^{(1)}(\mathbf{r},t)=\phi_{+1}^{(1)}(\mathbf{r})\exp(i\omega t)+\phi_{-1}^{(1)}(\mathbf{r})\exp(-i\omega t), \tag{87a}$$

$$\phi^{(2)}(\mathbf{r},t)=\phi_{+2}^{(2)}(\mathbf{r})\exp(i2\omega t)+\phi_{-2}^{(2)}(\mathbf{r})\exp(-i2\omega t)+\phi_0^{(2)}(\mathbf{r}), \tag{87b}$$

$$\phi^{(3)}(\mathbf{r},t)=\phi_{+3}^{(3)}(\mathbf{r})\exp(i3\omega t)+\phi_{-3}^{(3)}(\mathbf{r})\exp(-i3\omega t)+\phi_{+1}^{(3)}(\mathbf{r})\exp(i\omega t)+\phi_{-1}^{(3)}(\mathbf{r})\exp(-i\omega t)], \tag{87c}$$

where the spatial functions satisfy

$$[H^{(0)}(\mathbf{r})-E_0^{(0)}\pm\hbar\omega]\phi_{\pm1}^{(1)}(\mathbf{r})+[h^{(1)}(\mathbf{r})-\epsilon^{(1)}]\phi_0^{(0)}(\mathbf{r})=0, \qquad \epsilon^{(1)}=\langle\phi_0^{(0)}\mid h^{(1)}\mid\phi_0^{(0)}\rangle, \tag{88a}$$

$$[H^{(0)}(\mathbf{r})-E_0^{(0)}\pm2\hbar\omega]\phi_{\pm2}^{(2)}(\mathbf{r})+[h^{(1)}(\mathbf{r})-\epsilon^{(1)}]\phi_{\pm1}^{(1)}(\mathbf{r})=\epsilon_{\pm2}^{(2)}\phi_0^{(0)}(\mathbf{r}),$$

$$\epsilon_{\pm2}^{(2)}=\langle\phi_0^{(0)}\mid h^{(1)}\mid\phi_{\pm1}^{(1)}\rangle, \tag{88b}$$

$$[H^{(0)}(\mathbf{r})-E_0^{(0)}]\phi_0^{(2)}(\mathbf{r})+[h^{(1)}(\mathbf{r})-\epsilon^{(1)}][\phi_{+1}^{(1)}(\mathbf{r})+\phi_{-1}^{(1)}(\mathbf{r})]=\epsilon_0^{(2)}\phi_0^{(0)}(\mathbf{r}),$$

$$\epsilon_0^{(2)}=\epsilon_{+2}^{(2)}+\epsilon_{-2}^{(2)}, \tag{88c}$$

$$[H^{(0)}(\mathbf{r})-E_0^{(0)}\pm3\hbar\omega]\phi_{\pm3}^{(3)}(\mathbf{r})+[h^{(1)}(\mathbf{r})-\epsilon^{(1)}]\phi_{\pm2}^{(2)}(\mathbf{r})=\epsilon_{\pm2}^{(2)}\phi_{\pm1}^{(1)}(\mathbf{r})+\epsilon_{\pm3}^{(3)}\phi_0^{(0)}(\mathbf{r}),$$

$$\epsilon_{\pm3}^{(3)}=\langle\phi_0^{(0)}\mid h^{(1)}\mid\phi_{\pm2}^{(2)}\rangle, \tag{88d}$$

$$[H^{(0)}(\mathbf{r})-E_0^{(0)}\pm\hbar\omega]\phi_{\pm1}^{(3)}(\mathbf{r})+[h^{(1)}(\mathbf{r})-\epsilon^{(1)}][\phi_{\pm2}^{(2)}(\mathbf{r})+\phi_0^{(2)}(\mathbf{r})]=\epsilon_{\pm2}^{(2)}\phi_{\mp1}^{(1)}(\mathbf{r})+\epsilon_0^{(2)}\phi_{\pm1}^{(1)}(\mathbf{r})+\epsilon_{\pm1}^{(3)}\phi_0^{(0)}(\mathbf{r}),$$

$$\epsilon_{\pm1}^{(3)}=\epsilon_0^{(3)}+\epsilon_{\pm3}^{(3)}, \qquad \epsilon_0^{(3)}=\langle\phi_0^{(0)}\mid h^{(1)}\mid\phi_0^{(2)}\rangle, \tag{88e}$$

and we have made use of the expressions $(t\to+\infty)$

$$E^{(1)}(t)=\langle\phi_0^{(0)}\mid H^{(1)}\mid\phi_0^{(0)}\rangle=\epsilon^{(1)}[\exp(i\omega t)+\exp(-i\omega t)], \tag{89a}$$

$$E^{(2)}(t)=\langle\phi_0^{(0)}\mid H^{(1)}\mid\phi^{(1)}\rangle=\epsilon_{+2}^{(2)}\exp(i2\omega t)+\epsilon_{-2}^{(2)}\exp(-i2\omega t)+\epsilon_0^{(2)}, \tag{89b}$$

$$E^{(3)}(t)=\langle\phi_0^{(0)}\mid H^{(1)}\mid\phi^{(2)}\rangle=\epsilon_{+3}^{(3)}\exp(i3\omega t)+\epsilon_{-3}^{(3)}\exp(-i3\omega t)+\epsilon_{+1}^{(3)}\exp(i\omega t)+\epsilon_{-1}^{(3)}\exp(-i\omega t). \tag{89c}$$

To complete the evaluation of the wave function for a harmonic perturbation, we require explicit expressions for

[52] See, for example, Coddington and Levinson (1955).

[53] It is important to recognize that Eq. (85) is a second-order linear, inhomogeneous differential equation and, consequently, the two linearly independent solutions of the associated homogeneous equation can appear in the general solution. For $k\neq0$ and $k\hbar\omega\neq(E_i^{(0)}-E_0^{(0)})$ there are, however, no square-integrable homogeneous solutions. Consequently, for the perturbation of a bound state at applied frequency away from resonances, the homogeneous solutions cannot appear in the general solution. For $k=0$, $\phi_0^{(0)}(\mathbf{r})$ is a square-integrable homogeneous solution, but our normalization convention [Eq. (53c)] requires that it does not appear in any of the $\phi^{(n)}(\mathbf{r},t)$. In all cases, therefore, we need concern ourselves only with the particular solutions of Eq. (85) which contain no multiples of the homogeneous solutions. The homogeneous solutions of Eq. (85) in the case of atomic hydrogen are discussed by Alexander and Gordon (1971).

the integrals appearing in Eqs. (59). From Eqs. (89) and (61) we find $(t\rightarrow+\infty)$ [54]

$$(i\hbar)^{-1}\int_{-\infty}^{t}E^{(1)}(t')\,dt'=(i\hbar)^{-1}\epsilon^{(1)}\frac{2\sin\omega t}{\omega}, \tag{90a}$$

$$(i\hbar)^{-1}\int_{-\infty}^{t}E^{(2)}(t')\,dt'=(i\hbar)^{-1}\epsilon_0^{(2)}\left(t+\frac{\sin 2\omega t}{2\omega}\right)-\tfrac{1}{2}\langle\phi^{(1)}\mid\phi^{(1)}\rangle, \tag{90b}$$

$$(i\hbar)^{-1}\int_{-\infty}^{t}E^{(3)}(t')\,dt'=(i\hbar)^{-1}(\epsilon_{+3}^{(3)}+\epsilon_{-3}^{(3)})\frac{\sin 3\omega t}{3\omega}+(i\hbar)^{-1}(\epsilon_{+1}^{(3)}+\epsilon_{-1}^{(3)})\frac{\sin\omega t}{\omega}-\tfrac{1}{2}(\langle\phi^{(2)}\mid\phi^{(1)}\rangle+\langle\phi^{(1)}\mid\phi^{(2)}\rangle). \tag{90c}$$

Inserting Eqs. (90) into Eqs. (59), we obtain, to third order,

$$\Psi^{(0)}(\mathbf{r},t)=\phi_0^{(0)}(\mathbf{r})\exp[(i\hbar)^{-1}E_0^{(0)}t] \tag{91a}$$

$$\Psi^{(1)}(\mathbf{r},t)=[\phi^{(1)}(\mathbf{r},t)+(i\hbar)^{-1}\epsilon^{(1)}(2\sin\omega t/\omega)\phi_0^{(0)}(\mathbf{r})]\exp[(i\hbar)^{-1}E_0^{(0)}t] \tag{91b}$$

$$\begin{aligned}\Psi^{(2)}(\mathbf{r},t)=[&\phi^{(2)}(\mathbf{r},t)-\tfrac{1}{2}\langle\phi^{(1)}\mid\phi^{(1)}\rangle\phi_0^{(0)}(\mathbf{r})+(i\hbar)^{-1}\epsilon^{(1)}(2\sin\omega t/\omega)\phi^{(1)}(\mathbf{r},t)+(i\hbar)^{-1}\epsilon_0^{(2)}[t+(\sin 2\omega t/2\omega)]\phi_0^{(0)}(\mathbf{r})\\&+\tfrac{1}{2}(i\hbar)^{-2}[\epsilon^{(1)}(2\sin\omega t/\omega)]^2\phi_0^{(0)}(\mathbf{r})]\exp[(i\hbar)^{-1}E_0^{(0)}t],\end{aligned} \tag{91c}$$

$$\begin{aligned}\Psi^{(3)}(\mathbf{r},t)=[&\phi^{(3)}(\mathbf{r},t)-\tfrac{1}{2}\langle\phi^{(1)}\mid\phi^{(1)}\rangle\phi^{(1)}(\mathbf{r},t)-\tfrac{1}{2}(\langle\phi^{(1)}\mid\phi^{(2)}\rangle+\langle\phi^{(2)}\mid\phi^{(1)}\rangle)\phi_0^{(0)}(\mathbf{r})\\&+(i\hbar)^{-1}\epsilon^{(1)}(2\sin\omega t/\omega)[\phi^{(2)}(\mathbf{r},t)-\tfrac{1}{2}\langle\phi^{(1)}\mid\phi^{(1)}\rangle\phi_0^{(0)}(\mathbf{r})]+(i\hbar)^{-1}\epsilon_0^{(2)}[t+(\sin 2\omega t/2\omega)]\phi^{(1)}(\mathbf{r},t)\\&+(i\hbar)^{-1}(\epsilon_{+3}^{(3)}+\epsilon_{-3}^{(3)})(\sin 3\omega t/3\omega)\phi_0^{(0)}(\mathbf{r})+(i\hbar)^{-1}(\epsilon_{+1}^{(3)}+\epsilon_{-1}^{(3)})(\sin\omega t/\omega)\phi_0^{(0)}(\mathbf{r})\\&+\tfrac{1}{2}(i\hbar)^{-2}[\epsilon^{(1)}(2\sin\omega t/\omega)]^2\phi^{(1)}(\mathbf{r},t)+(i\hbar)^{-2}[\epsilon^{(1)}(2\sin\omega t/\omega)]\epsilon_0^{(2)}[t+(\sin 2\omega t/2\omega)]\phi_0^{(0)}(\mathbf{r})\\&+\tfrac{1}{6}(i\hbar)^{-3}[\epsilon^{(1)}(2\sin\omega t/\omega)]^3\phi_0^{(0)}(\mathbf{r})]\exp[(i\hbar)^{-1}E_0^{(0)}t].\end{aligned} \tag{91d}$$

Equations (91) explicitly exhibit both the normalization and secular terms that arise in the Schrödinger perturbation functions for harmonic perturbations. We write them out in detail here in order to facilitate subsequent comparison with the Dirac approach, whereas it is generally convenient to incorporate the secular terms appearing in Eqs. (91) into an overall phase factor, as in Eqs. (33) and (40). The complete wave function, through third order, then takes the more compact form

$$\begin{aligned}\Psi(\mathbf{r},t)=\{&\phi_0^{(0)}(\mathbf{r})+\phi^{(1)}(\mathbf{r},t)+\phi^{(2)}(\mathbf{r},t)-\tfrac{1}{2}\langle\phi^{(1)}\mid\phi^{(1)}\rangle\phi_0^{(0)}(\mathbf{r})+\phi^{(3)}(\mathbf{r},t)-\tfrac{1}{2}\langle\phi^{(1)}\mid\phi^{(1)}\rangle\phi^{(1)}(\mathbf{r},t)-\tfrac{1}{2}(\langle\phi^{(2)}\mid\phi^{(1)}\rangle\\&+\langle\phi^{(1)}\mid\phi^{(2)}\rangle)\phi_0^{(0)}(\mathbf{r})+\cdots\}\exp\big((i\hbar)^{-1}\{E_0^{(0)}t+\epsilon^{(1)}(2\sin\omega t/\omega)+\epsilon_0^{(2)}[t+(\sin 2\omega t/2\omega)]\\&+(\epsilon_{-3}^{(3)}+\epsilon_{+3}^{(3)})(\sin 3\omega t/3\omega)+(\epsilon_{+1}^{(3)}+\epsilon_{-1}^{(3)})(\sin\omega t/\omega)+\cdots\}\big),\end{aligned} \tag{92}$$

where we have retained the expansion of the normalization terms by making use of Eq. (40) rather than Eq. (33). We see that both linear and oscillatory time-dependent terms appear in the phase factor of Eq. (92). In the expansion of this phase factor [Eqs. (91)], the former produce secular divergent terms while the latter result in oscillatory secular terms in the functions $\Psi^{(n)}(\mathbf{r},t)$. In the static limit, $\omega\rightarrow 0$, the oscillatory terms become linear in $t$ (i.e., secular divergent) and, consequently, their incorporation in the phase of Eq. (92) is essential for a uniform passage to the time-independent case in which the correct static energy shift is obtained. If only the secular divergent terms in Eqs. (91) (i.e., those involving $\epsilon_0^{(2)}t$) were incorporated into a phase factor for $\omega\neq 0$, and then the limit $\omega\rightarrow 0$ were taken, an incorrect static energy shift would appear in the phase factor. Further, secular divergent terms would be present in the perturbation functions [Eqs. (91)]; i.e., in the limit $\omega\rightarrow 0$, part of the static energy shift would appear as a phase factor and part in expanded form as secular divergent terms. Moreover, it is important to recognize that the oscillatory terms in the phase factor of Eq. (92) arise from cancellations between individual terms; e.g., $\sin\omega t/\omega$ arises from $\exp(i\omega t)/\omega$ and $\exp(-i\omega t)/\omega$. In the static limit $\omega\rightarrow 0$, the individual terms diverge and produce the secular divergent behavior only when properly combined. Since finding the proper combinations becomes somewhat involved in higher-order, it is well to isolate such terms once and for all in the phase factor of Eqs. (33) or (40); this avoids any possibility of an irregular wave function for $\omega\rightarrow 0$.

Solutions of Eqs. (88) can be obtained by variational techniques or by expanding the perturbation functions in the complete set of eigenfunctions of $H^{(0)}(\mathbf{r})$ (see

[54] We employ the switching function of Eqs. (72) and (73) discussed in Footnote 49.

Appendix A). The expressions resulting from the latter approach are in a form suitable for comparison with the perturbation functions obtained using the Dirac variation-of-constants method [Eqs. (14) and (17)]. Such a comparison makes it possible to identify the sources in the Dirac method of the normalization and secular terms explicitly exhibited in Eqs. (91) and serves to emphasize that these solutions are merely a particular grouping of the variation-of-constants results.

To obtain the Dirac variation-of-constants solution, we introduce the adiabatically switched-on harmonic perturbation of Eq. (80) into Eqs. (14).[54] Restricting attention to the time interval subsequent to switching ($t\rightarrow+\infty$), we obtain from Eqs. (14) for $n=1$

$$a_k^{(1)}(t)=(\hbar)^{-1}\langle\phi_k^{(0)}\mid h^{(1)}\mid\phi_0^{(0)}\rangle(\{\exp[i(\omega+\omega_{k0})t]/(\omega_{k0}+\omega)\}+\{\exp[-i(\omega-\omega_{k0})t/(\omega_{k0}-\omega)\}), \tag{93}$$

valid for all $k$. Inserting this result into Eq. (17) for $n=1$ gives an expression for the first-order perturbation function. Comparison of this function with Eqs. (87a) and (91b) shows that

$$\phi_{\pm1}^{(1)}(\mathbf{r})=-(\hbar)^{-1}\sum_{k\neq0}^{\infty}\frac{\langle\phi_k^{(0)}\mid h^{(1)}\mid\phi_0^{(0)}\rangle}{(\omega_{k0}\pm\omega)}\phi_k^{(0)}(\mathbf{r}), \tag{94}$$

which is in agreement with the solution of Eq. (88a) given in Appendix A [Eqs. (A1) and (A8)]. Further, the $a_0^{(1)}(t)$ value obtained from Eq. (93) is seen to be in agreement with Eqs. (90a) and (91b).

Proceeding to the second-order case, we find that Eqs. (14) for $n=2$ give the results, valid in the limit $t\rightarrow+\infty$,

$$a_k^{(2)}(t)=(\hbar)^{-2}\sum_{l=0}^{\infty}\langle\phi_k^{(0)}\mid h^{(1)}\mid\phi_l^{(0)}\rangle\langle\phi_l^{(0)}\mid h^{(1)}\mid\phi_0^{(0)}\rangle\left(\frac{\exp[i(2\omega+\omega_{k0})t]}{(2\omega+\omega_{k0})(\omega+\omega_{l0})}+\frac{\exp[-i(2\omega-\omega_{k0})t]}{(2\omega-\omega_{k0})(\omega-\omega_{l0})}\right.$$
$$\left.+\frac{\exp(i\omega_{k0}t)}{\omega_{k0}}[(\omega+\omega_{l0})^{-1}-(\omega-\omega_{l0})^{-1}]\right),\qquad k\neq0 \tag{95a}$$

$$a_0^{(2)}(t)=(\hbar)^{-2}\sum_{l=0}^{\infty}|\langle\phi_l^{(0)}\mid h^{(1)}\mid\phi_0^{(0)}\rangle|^2\left(\frac{\exp(i2\omega t)}{2\omega(\omega+\omega_{l0})}+\frac{\exp(-i2\omega t)}{2\omega(\omega-\omega_{l0})}+\frac{it}{(\omega+\omega_{l0})}-\frac{it}{(\omega-\omega_{l0})}\right.$$
$$\left.-\tfrac{1}{2}(\omega+\omega_{l0})^{-2}-\tfrac{1}{2}(\omega-\omega_{l0})^{-2}\right). \tag{95b}$$

Use of these expressions in Eq. (17) for $n=2$ yields the second-order function and comparison with Eqs. (87b) and (91c) permits one to identify each of the terms in $\Psi^{(2)}(\mathbf{r},t)$. The $l=0$ term in Eq. (95b) gives

$$(\hbar)^{-2}/2\omega^2\,|\langle\phi_0^{(0)}\mid h^{(1)}\mid\phi_0^{(0)}\rangle|^2[\exp(i2\omega t)+\exp(-i2\omega t)-2]=\tfrac{1}{2}(i\hbar)^{-2}\left(\int_{-\infty}^{t}E^{(1)}(t')\,dt'\right)^2, \tag{96}$$

the coefficient of the last term in Eq. (91c) [see Eq. (90a)], while the rest of the sum in Eq. (95b) leads to the remaining terms proportional to $\phi_0^{(0)}(\mathbf{r})$. Separating these into real and imaginary parts, we have

$$(\hbar)^{-2}\sum_{l\neq0}^{\infty}|\langle\phi_l^{(0)}\mid h^{(1)}\mid\phi_0^{(0)}\rangle|^2\left(\frac{\exp(i2\omega t)}{2\omega(\omega+\omega_{l0})}+\frac{\exp(-i2\omega t)}{2\omega(\omega-\omega_{l0})}+\frac{it}{(\omega+\omega_{l0})}-\frac{it}{(\omega-\omega_{l0})}-\tfrac{1}{2}(\omega+\omega_{l0})^{-2}-\tfrac{1}{2}(\omega-\omega_{l0})^{-2}\right)$$
$$=-i(\hbar)^{-2}\sum_{l\neq0}^{\infty}\frac{2\omega_{l0}\,|\langle\phi_l^{(0)}\mid h^{(1)}\mid\phi_0^{(0)}\rangle|^2}{(\omega^2-\omega_{l0}^2)}\left(t+\frac{\sin2\omega t}{2\omega}\right)-\tfrac{1}{2}(\hbar)^{-2}\sum_{l\neq0}^{\infty}|\langle\phi_l^{(0)}\mid h^{(1)}\mid\phi_0^{(0)}\rangle|^2$$
$$\times\left((\omega+\omega_{l0})^{-2}+(\omega-\omega_{l0})^{-2}-\frac{\cos2\omega t}{\omega}[(\omega+\omega_{l0})^{-1}+(\omega-\omega_{l0})^{-1}]\right)$$
$$=(i\hbar)^{-1}\epsilon_0^{(2)}[t+(\sin2\omega t/2\omega)]-\tfrac{1}{2}\langle\phi^{(1)}\mid\phi^{(1)}\rangle$$
$$=(i\hbar)^{-1}\int_{-\infty}^{t}E^{(2)}(t')\,dt', \tag{97}$$

from Eq. (90b), with

$$\epsilon_0^{(2)} = \langle \phi_0^{(0)} \mid h^{(1)} \mid \phi_{+1}^{(1)} \rangle + \langle \phi_0^{(0)} \mid h^{(1)} \mid \phi_{-1}^{(1)} \rangle$$

$$= -(\hbar)^{-1} \sum_{l \neq 0}^{\infty} \frac{2\omega_{l0} \mid \langle \phi_l^{(0)} \mid h^{(1)} \mid \phi_0^{(0)} \rangle \mid^2}{(\omega_{l0}^2 - \omega^2)} . \tag{98}$$

The part of $\Psi^{(2)}(\mathbf{r}, t)$ orthogonal to $\phi_0^{(0)}(\mathbf{r})$ arises from Eq. (95a), which can be rewritten

$$a_k^{(2)}(t) = \Bigg[ (\hbar)^{-2} \sum_{l \neq 0}^{\infty} \langle \phi_k^{(0)} \mid h^{(1)} \mid \phi_l^{(0)} \rangle \langle \phi_l^{(0)} \mid h^{(1)} \mid \phi_0^{(0)} \rangle \Bigg( \frac{\exp[i(2\omega + \omega_{k0})t]}{(2\omega + \omega_{k0})(\omega + \omega_{l0})} + \frac{\exp[-i(2\omega - \omega_{k0})t]}{(2\omega - \omega_{k0})(\omega - \omega_{l0})}$$

$$+ \frac{\exp(i\omega_{k0}t)}{\omega_{k0}} [(\omega + \omega_{l0})^{-1} - (\omega - \omega_{l0})^{-1}] \Bigg) - (\hbar)^{-2} \langle \phi_k^{(0)} \mid h^{(1)} \mid \phi_0^{(0)} \rangle \langle \phi_0^{(0)} \mid h^{(1)} \mid \phi_0^{(0)} \rangle \Bigg( \frac{\exp[i(2\omega + \omega_{k0})t]}{(2\omega + \omega_{k0})(\omega + \omega_{k0})}$$

$$+ \frac{\exp[-i(2\omega - \omega_{k0})t]}{(2\omega - \omega_{k0})(\omega - \omega_{k0})} - \omega_{k0}^{-1} [(\omega - \omega_{k0})^{-1} - (\omega + \omega_{k0})^{-1}] \Bigg) \Bigg] + \Bigg[ (\hbar)^{-2} \langle \phi_k^{(0)} \mid h^{(1)} \mid \phi_0^{(0)} \rangle \langle \phi_0^{(0)} \mid h^{(1)} \mid \phi_0^{(0)} \rangle$$

$$\times \Bigg\{ \frac{\exp[i(2\omega + \omega_{k0})t]}{\omega(\omega + \omega_{k0})} + \frac{\exp[-i(2\omega - \omega_{k0})t]}{\omega(\omega - \omega_{k0})} - \frac{\exp[i\omega_{k0}t]}{\omega} [(\omega + \omega_{k0})^{-1} + (\omega - \omega_{k0})^{-1}] \Bigg\} \Bigg], \qquad k \neq 0. \tag{99}$$

It can be seen that the term in the first large square bracket corresponds to $\phi^{(2)}(\mathbf{r}, t)$, while that in the second gives rise to the third term in Eq. (91c), in agreement with Eqs. (87b), (A2), (A3), (A9), and (A10).

From the foregoing analysis, it is clear that the functions of Eqs. (91b) and (91c) are particular groupings of the Dirac variation-of-constants solutions which make evident the presence of secular and normalization terms. Although this is perfectly clear in general from the development of Sec. II, it is reassuring to make explicit comparisons in first- and second-order. Corresponding comparisons in the third- and higher-order cases can also be carried out, although the expressions become somewhat unwieldy and are not reproduced here. However, the spectral solutions of Eqs. (88) are given in Appendix A for convenient reference.

### D. Electric Dipole Polarization

We apply the results obtained for an adiabatically switched-on harmonic perturbation to a system perturbed by monochromatic radiation in the uniform-electric-field approximation.[19] The appropriate perturbation operator is $(t \rightarrow +\infty)$

$$H^{(1)}(\mathbf{r}, t) = -e \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{E}^{(\omega)} \cos \omega t, \tag{100}$$

which can be rewritten

$$H^{(1)}(r, t) = \lambda h^{(1)}(\mathbf{r}) [\exp(i\omega t) + \exp(-i\omega t)], \tag{101}$$

with

$$\lambda = (E^{(\omega)}/2) \tag{102a}$$

$$h^{(1)}(\mathbf{r}) = -e \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{a} \equiv -e\mathbf{r} \cdot \mathbf{a}. \tag{102b}$$

Here, $N$ is the number of electrons in the system, $E^{(\omega)} = \mid \mathbf{E}^{(\omega)} \mid$ is the (constant) amplitude of the electric field, $\mathbf{a}$ is a unit vector in its polarization direction, $e$ is the (negative) electronic charge, and the perturbation parameter $\lambda$ is introduced for convenience. When the perturbation equations [Eqs. (88)] are solved for the perturbation of Eq. (102b), the resulting time-dependent functions $\Psi^{(n)}(\mathbf{r}, t)$ are given by Eqs. (91), modified to include the perturbation parameter $\lambda$, and the complete wave function through third order is given by Eq. (92).[55]

The induced electronic dipole moment

$$\boldsymbol{\mu}(t) = e\langle \Psi \mid \mathbf{r} \mid \Psi \rangle \tag{103}$$

can be obtained to third-order from Eqs. (91) and (92).

[55] The total wave function through third order [Eq. (92)] includes a second-order term $\lambda^2 \epsilon_0^{(2)}$ in the phase factor which represents a shift of the unperturbed energy level (see Footnote 10). We recognize this as the dynamic Stark shift (see Footnote 11), proportional to the dynamic (frequency dependent) polarizability $[\alpha(\omega) = \epsilon_0^{(2)}]$, which is given by the familiar Kramers–Heisenberg formula [Eqs. (98) and (102a)]. Such light shifts in optical transitions apparently have been observed by Aleksandrov *et al.* (1966). See also, Bonch-Bruevich and Khodovoi (1968). Related light shifts in pumping experiments have been investigated by Arditi and Carver (1961), Cohen-Tannoudji (1961), van der Ziel, Pershan, and Malmstrom (1965), Pershan, van der Ziel, and Malmstrom (1966), Happer and Mathur (1967b), and Khadjavi, Lurio, and Happer (1968).

We find[56]

$$\langle\Psi \mid \mathbf{r} \mid \Psi\rangle = \mathbf{P}_0^{(0)} + \mathbf{P}_\omega^{(1)} E^{(\omega)} \cos\omega t + \mathbf{P}_0^{(2)} (E^{(\omega)})^2 + \mathbf{P}_{2\omega}^{(2)} (E^{(\omega)})^2 \cos 2\omega t + \mathbf{P}_\omega^{(3)} (E^{(\omega)})^3 \cos\omega t + \mathbf{P}_{3\omega}^{(3)} (E^{(\omega)})^3 \cos 3\omega t, \tag{104}$$

where, with all functions real,

$$\mathbf{P}_0^{(0)} = \langle\phi_0^{(0)} \mid \mathbf{r} \mid \phi_0^{(0)}\rangle \tag{105a}$$

$$\mathbf{P}_\omega^{(1)} = \langle\phi_0^{(0)} \mid \mathbf{r} \mid \phi_{+1}^{(1)}\rangle + \langle\phi_{-1}^{(1)} \mid \mathbf{r} \mid \phi_0^{(0)}\rangle \tag{105b}$$

$$\mathbf{P}_0^{(2)} = \tfrac{1}{4}[\langle\phi_0^{(0)} \mid \mathbf{r} \mid \phi_0^{(2)}\rangle + \langle\phi_0^{(2)} \mid \mathbf{r} \mid \phi_0^{(0)}\rangle + \langle\phi_{+1}^{(1)} \mid \mathbf{r} \mid \phi_{+1}^{(1)}\rangle + \langle\phi_{-1}^{(1)} \mid \mathbf{r} \mid \phi_{-1}^{(1)}\rangle - \langle\phi_0^{(0)} \mid \mathbf{r} \mid \phi_0^{(0)}\rangle(\langle\phi_{+1}^{(1)} \mid \phi_{+1}^{(1)}\rangle + \langle\phi_{-1}^{(1)} \mid \phi_{-1}^{(1)}\rangle)] \tag{105c}$$

$$\mathbf{P}_{2\omega}^{(2)} = \tfrac{1}{2}[\langle\phi_0^{(0)} \mid \mathbf{r} \mid \phi_{+2}^{(2)}\rangle + \langle\phi_{-2}^{(2)} \mid \mathbf{r} \mid \phi_0^{(0)}\rangle + \langle\phi_{-1}^{(1)} \mid \mathbf{r} \mid \phi_{+1}^{(1)}\rangle - \langle\phi_0^{(0)} \mid \mathbf{r} \mid \phi_0^{(0)}\rangle\langle\phi_{-1}^{(1)} \mid \phi_{+1}^{(1)}\rangle], \tag{105d}$$

$$\mathbf{P}_\omega^{(3)} = \tfrac{1}{4}[\langle\phi_0^{(0)} \mid \mathbf{r} \mid \phi_{+1}^{(3)}\rangle + \langle\phi_{-1}^{(3)} \mid \mathbf{r} \mid \phi_0^{(0)}\rangle + \langle\phi_{+1}^{(1)} \mid \mathbf{r} \mid \phi_{+2}^{(2)}\rangle + \langle\phi_{-2}^{(2)} \mid \mathbf{r} \mid \phi_{-1}^{(1)}\rangle + \langle\phi_0^{(2)} \mid \mathbf{r} \mid \phi_{+1}^{(1)}\rangle + \langle\phi_{-1}^{(1)} \mid \mathbf{r} \mid \phi_0^{(2)}\rangle - \langle\phi_0^{(0)} \mid \mathbf{r} \mid \phi_0^{(0)}\rangle(\langle\phi_{+1}^{(1)} \mid \phi_{+2}^{(2)}\rangle + \langle\phi_{-2}^{(2)} \mid \phi_{-1}^{(1)}\rangle + \langle\phi_0^{(2)} \mid \phi_{+1}^{(1)}\rangle + \langle\phi_{-1}^{(1)} \mid \phi_0^{(2)}\rangle) - (\langle\phi_{+1}^{(1)} \mid \mathbf{r} \mid \phi_0^{(0)}\rangle + \langle\phi_0^{(0)} \mid \mathbf{r} \mid \phi_{-1}^{(1)}\rangle)(\langle\phi_{-1}^{(1)} \mid \phi_{+1}^{(1)}\rangle + \langle\phi_{+1}^{(1)} \mid \phi_{+1}^{(1)}\rangle + \langle\phi_{-1}^{(1)} \mid \phi_{-1}^{(1)}\rangle)] \tag{105e}$$

$$\mathbf{P}_{3\omega}^{(3)} = \tfrac{1}{4}[\langle\phi_0^{(0)} \mid \mathbf{r} \mid \phi_{+3}^{(3)}\rangle + \langle\phi_{-3}^{(3)} \mid \mathbf{r} \mid \phi_0^{(0)}\rangle + \langle\phi_{-1}^{(1)} \mid \mathbf{r} \mid \phi_{+2}^{(2)}\rangle + \langle\phi_{-2}^{(2)} \mid \mathbf{r} \mid \phi_{+1}^{(1)}\rangle - \langle\phi_0^{(0)} \mid \mathbf{r} \mid \phi_0^{(0)}\rangle(\langle\phi_{-2}^{(2)} \mid \phi_{+1}^{(1)}\rangle + \langle\phi_{-1}^{(1)} \mid \phi_{+2}^{(2)}\rangle) - \langle\phi_{-1}^{(1)} \mid \phi_{+1}^{(1)}\rangle(\langle\phi_0^{(0)} \mid \mathbf{r} \mid \phi_{+1}^{(1)}\rangle + \langle\phi_{-1}^{(1)} \mid \mathbf{r} \mid \phi_0^{(0)}\rangle)]. \tag{105f}$$

The terms appearing in Eqs. (104) and (105) have simple physical interpretations and can be compared with previously obtained results.[2,5,6] The first and second terms in Eq. (104) are the static and first-order induced dipole moments, respectively, with the linear dipole polarizability given by Eq. (105b).[2] The third term in Eq. (104), a static moment quadratic in the field, gives rise to optical rectification or a.c. polarization.[57] The expression for $\mathbf{P}_0^{(2)}$ in Eq. (105c) is in disagreement with the previous results of Ward,[6] and Dalgarno,[2] due to the presence of the last term in Eq. (105c), which arises from the second-order normalization and appears to be missing from their formula[58]; this term evidently vanishes if the static moment is zero. The fourth term in Eq. (104), quadratic in the field, is responsible for second-harmonic generation.[59] Our expression for $\mathbf{P}_{2\omega}^{(2)}$ [Eq. (105d)] is the same as that of Ward and Dalgarno but their induced moment is out of phase with the external electric field while the present calculation gives a moment that is in phase, in agreement with an earlier result.[60] The fifth term in Eq. (104), cubic in the field, is responsible for the field dependence of the polarizability.[61] The coefficient $\mathbf{P}_\omega^{(3)}$ [Eq. (105c)], which is the dipole hyperpolarizability, is in disagreement with the Ward and Dalgarno result due to their improper normalization. Finally, the last term in Eq. (104), cubic in the field, is responsible for third-harmonic generation[62]; our coefficient, Eq. (105f), is in agreement with Ward and Dalgarno.[63]

The susceptibilities of Eqs. (105) are appropriate for computation employing variational procedures to determine the required functions $\phi_k^{(n)}(\mathbf{r})$ [Eqs. (88)].[64] By contrast, the expressions that result from Eqs. (105) when the customary spectral sums are introduced for the functions $\phi_k^{(n)}(\mathbf{r})$ (see Appendix A) are somewhat

[56] The induced electric dipole moment of Eqs. (104) and (105) is appropriate for a single isolated system, with $E^{(\omega)}$ the strength of the effective perturbing field. We do not consider here questions related to the determination of internal fields in condensed matter. Moreover, the perturbation Hamiltonian of Eqs. (100)–(102) is appropriate only for a single monochromatic incident wave as are, consequently, the susceptibilities of Eqs. (105). When two or more waves are present, it is of course necessary to specify their frequencies, amplitudes, polarizations, and relative phases in the perturbation Hamiltonian. In such cases, the susceptibilities of Eqs. (105) are replaced by more complex expressions involving cross terms which depend on various wave combinations and are not reproduced here.

[57] See, for example, Bass, Franken, Ward, and Weinreich (1962).

[58] Concerning modification of the expressions obtained by Ward (1965), see also, Bogaard, Buckingham, and Orr (1967), Sitz and Yaris (1968), Dana (1969), and Orr and Ward (1971).

[59] See, for example, Boyd, Ashkin, Dziedzii, and Kleinman (1965), Rez (1968), and Sitz and Yaris (1968).

[60] See, for example, Armstrong, Bloembergen, Ducuing, and Pershan (1962).

[61] See, for example, Boyle, Buckingham, Disch, and Dunmur (1966), Boyle and Coulson (1966, 1967), and Bogaard, Buckingham, and Orr (1967).

[62] See, for example, New and Ward (1967), Dawes (1968), Sitz and Yaris (1968), and Ward and New (1969).

[63] The failure of Ward's procedure (Footnote 6) to produce the proper normalization terms is apparently related to the fact that the Lippmann–Schwinger equation, upon which his diagrammatic analysis is based, does not provide a normalized wave function in the presence of a level shift. See, for example, Roman (1965) p. 342, for discussion of this point. We thank Professor Ward for informing us that the diagrammatic technique can be reinterpreted, and the proper normalization terms thereby obtained, along the lines suggested by Orr and Ward (1971).

[64] Following the development of Dalgarno (1966), the second-order functions appearing in Eqs. (105c) and (105d), and the third-order functions in Eqs. (105e) and (105f), can be eliminated in favor of new first-order functions satisfying Eq. (91b) with $\pm\hbar\omega$ replaced by 0, $\pm 2\hbar\omega$, and $\pm 3\hbar\omega$, respectively. This result is in accord with the general $2n+1$ theorem discussed by Epstein (1969), which we further consider in Sec. V.B.

cumbersome. The latter expressions, however, make explicit the frequency dependence of the susceptibilities and can be evaluated approximately by employing closure procedures. We tabulate the susceptibilities of Eqs. (105) in the customary forms of infinite sums in Appendix B for convenient reference and for comparison with previous results.[2,6]

### E. The Uncoupled Hartree–Fock Approximation

To illustrate the significance of the general development in computational applications of time-dependent perturbation theory, we consider here the proper formulation of the so-called uncoupled form of Hartree–Fock perturbation theory and contrast our results with those previously obtained.[2,10,65]

In the Hartree–Fock approximation, the unperturbed eigenfunction is written as a single Slater determinant[66]

$$\phi_{\mathrm{HF}}^{(0)}(\mathbf{r}) = (N!)^{-1/2} \det | u_1^{(0)}(\mathbf{r}_1) u_2^{(0)}(\mathbf{r}_2) \cdots u_N^{(0)}(\mathbf{r}_N) | \tag{106}$$

composed of $N$ unperturbed orthonormal Hartree–Fock spin–orbitals $u_i^{(0)}(\mathbf{r}_i)$. This function satisfies the zeroth-order Hartree–Fock equation

$$[H_{\mathrm{HF}}^{(0)}(\mathbf{r}) - E_{\mathrm{HF}}^{(0)}]\phi_{\mathrm{HF}}^{(0)}(\mathbf{r}) = 0, \tag{107}$$

where

$$H_{\mathrm{HF}}^{(0)}(\mathbf{r}) = \sum_{i=1}^{N} [h^{(0)}(\mathbf{r}_i) - \tfrac{1}{2} \sum_{j=1}^{N} \langle u_i^{(0)} u_j^{(0)} | (e^2/r_{ij}) \times (1 - P_{ij}) | u_i^{(0)} u_j^{(0)} \rangle], \tag{108a}$$

and

$$E_{\mathrm{HF}}^{(0)} = \sum_{i=1}^{N} [\epsilon_i^{(0)} - \tfrac{1}{2} \sum_{j=1}^{N} \langle u_i^{(0)} u_j^{(0)} | (e^2/r_{ij})(1 - P_{ij}) \times | u_i^{(0)} u_j^{(0)} \rangle] \tag{108b}$$

are the zeroth-order Hamiltonian and energy, respectively, and $P_{ij}$ is the permutation operator for the coordinates of electrons $i$ and $j$. We employ the standard notation for the two-electron integrals appearing in Eqs. (108), which are introduced to insure that the Coulomb repulsion energy between electrons does not appear twice in the total Hartree–Fock energy, and that the latter equals the expectation value of the (Coulombic) Hamiltonian over the Hartree–Fock wave function.[66] For an $N$-electron atom with atomic number $Z$, the Fock operator $h^{(0)}(\mathbf{r}_i)$ is

$$h^{(0)}(\mathbf{r}_i) = -(\hbar^2/2m)\nabla_i^2 - (Ze^2/r_i) + v^{(0)}(\mathbf{r}_i), \tag{109a}$$

where

$$v^{(0)}(\mathbf{r}_i) = \sum_{j=1}^{N} \langle u_j^{(0)} | (e^2/r_{ij})(1 - P_{ij}) | u_j^{(0)} \rangle \tag{109b}$$

is the nonlocal Fock potential. The Hartree–Fock spin–orbitals $u_i^{(0)}(\mathbf{r}_i)$ satisfy the equations

$$[h^{(0)}(\mathbf{r}_i) - \epsilon_i^{(0)}] u_i^{(0)}(\mathbf{r}_i) = 0, \tag{110a}$$

with the Hartree–Fock orbital energies given by

$$\epsilon_i^{(0)} = \langle u_i^{(0)} | h^{(0)} | u_i^{(0)} \rangle. \tag{110b}$$

The uncoupled Hartree–Fock approximation to the equations of time-dependent perturbation theory is obtained by replacing the unperturbed wave function, Hamiltonian, and energy in Eqs. (53) by their zeroth-order Hartree–Fock counterparts [Eqs. (106) and (108)];

$$\phi_0^{(0)}(\mathbf{r}) \to \phi_{\mathrm{HF}}^{(0)}(\mathbf{r}), \tag{111a}$$

$$H_0^{(0)}(\mathbf{r}) \to H_{\mathrm{HF}}^{(0)}(\mathbf{r}), \tag{111b}$$

$$E_0^{(0)} \to E_{\mathrm{HF}}^{(0)}. \tag{111c}$$

The first-order perturbation equation [Eq. (53a)] becomes

$$[H_{\mathrm{HF}}^{(0)}(\mathbf{r}) - E_{\mathrm{HF}}^{(0)} - i\hbar(\partial/\partial t)]\phi^{(1)}(\mathbf{r}, t) + [H^{(1)}(\mathbf{r}, t) - E^{(1)}(t)]\phi_{\mathrm{HF}}^{(0)}(\mathbf{r}) = 0, \tag{112}$$

where

$$[H_{\mathrm{HF}}^{(0)}(\mathbf{r}) - E_{\mathrm{HF}}^{(0)}] = \sum_{i=1}^{N} [h^{(0)}(\mathbf{r}_i) - \epsilon_i^{(0)}] \tag{113}$$

from Eqs. (108). Restricting attention to a perturbation in the form of a sum of one-electron operators,[67]

$$H^{(1)}(\mathbf{r}, t) = \sum_{i=1}^{N} g^{(1)}(\mathbf{r}_i, t), \tag{114}$$

we see that $E^{(1)}(t)$ is

$$E^{(1)}(t) \to E_{\mathrm{HF}}^{(1)}(t) = \langle \phi_{\mathrm{HF}}^{(0)} | H^{(1)} | \phi_{\mathrm{HF}}^{(0)} \rangle = \sum_{i=1}^{N} \langle u_i^{(0)} | g^{(1)} | u_i^{(0)} \rangle \equiv \sum_{i=1}^{N} \epsilon_i^{(1)}(t). \tag{115}$$

Since the $N$-electron operators in Eq. (112) are sums of one-electron operators, a separation, or uncoupling, of Eq. (112) can be effected in this approximation by introducing the ansatz

$$\phi^{(1)}(\mathbf{r}, t) \to \phi_{\mathrm{HF}}^{(1)}(\mathbf{r}, t) = \sum_{i=1}^{N} U_i^{(1)}(\mathbf{r}, t) \tag{116}$$

with

$$U_i^{(1)}(\mathbf{r}, t) = (N!)^{-1/2} \times \det | u_1^{(0)}(\mathbf{r}_1) u_2^{(0)}(\mathbf{r}_2) \cdots u_{i-1}^{(0)}(\mathbf{r}_{i-1}) \; u_i^{(1)}(\mathbf{r}_i, t) u_{i+1}^{(0)}(\mathbf{r}_{i+1}) \cdots u_N^{(0)}(\mathbf{r}_N) |. \tag{117}$$

We recognize Eq. (117) as the Slater determinant obtained from $\phi_{\mathrm{HF}}^{(0)}(\mathbf{r})$ by replacing $u_i^{(0)}(\mathbf{r}_i)$ with the first-order spin–orbital $u_i^{(1)}(\mathbf{r}, t)$. In terms of these spin–orbitals, the orthogonality requirement [Eq.

[65] See Dalgarno (1959, 1962), and references cited therein, for discussion of the analogous approximation in the case of a static perturbation.

[66] For a discussion of Hartree–Fock theory applied to the electronic structure of atoms and molecules see, for example, Slater (1960).

[67] This particular form of perturbation Hamiltonian is especially appropriate for the interaction of radiation and matter [Eq. (100)]. A corresponding formalism can also be developed for a two-electron perturbation Hamiltonian, although we do not treat this case here.

(53c), $n=1$]

$$\langle\phi^{(0)} \mid \phi^{(1)}\rangle \rightarrow \langle\phi_{\mathrm{HF}}{}^{(0)} \mid \phi_{\mathrm{HF}}{}^{(1)}\rangle = 0, \tag{118}$$

becomes

$$\sum_{i=1}^{N} \langle\phi_{\mathrm{HF}}{}^{(0)} \mid U_i{}^{(1)}\rangle = \sum_{i=1}^{N} \langle u_i{}^{(0)} \mid u_i{}^{(1)}\rangle = 0. \tag{119}$$

Substituting Eq. (116) into Eq. (112), we find that the latter will be satisfied if we require the first-order spin–orbitals to be solutions of

$$[h^{(0)}(\mathbf{r}_i) - \epsilon_i{}^{(0)} - i\hbar(\partial/\partial t)]u_i{}^{(1)}(\mathbf{r}_i, t) + [g^{(1)}(\mathbf{r}_i, t) - \epsilon_i{}^{(1)}(t)]u_i{}^{(0)}(\mathbf{r}_i) = 0. \tag{120}$$

This is the canonical form of the differential equation to be satisfied by the first-order perturbed spin–orbital, $u_i{}^{(1)}(\mathbf{r}_i, t)$. It is an immediate consequence of Eq. (120) that

$$i\hbar(\partial/\partial t)\langle u_i{}^{(0)} \mid u_i{}^{(1)}\rangle = 0, \tag{121a}$$

and

$$i\hbar(\partial/\partial t)[\langle u_j{}^{(0)} \mid u_i{}^{(1)}\rangle + \langle u_j{}^{(1)} \mid u_i{}^{(0)}\rangle] = (\epsilon_j{}^{(0)} - \epsilon_i{}^{(0)})[\langle u_j{}^{(0)} \mid u_i{}^{(1)}\rangle + \langle u_j{}^{(1)} \mid u_i{}^{(0)}\rangle]. \tag{121b}$$

From Eq. (121a) we see, since $u_i{}^{(1)}(\mathbf{r}_i, t) = 0$ initially, that $\langle u_i{}^{(0)} \mid u_i{}^{(1)}\rangle$ will vanish for all $t$ and thus Eq. (119) will be satisfied by the solutions of Eq. (120). Further, we see from Eq. (121b) that since $\langle u_j{}^{(0)} \mid u_i{}^{(1)}\rangle + \langle u_j{}^{(1)} \mid u_i{}^{(0)}\rangle$ vanishes initially, it will also vanish for all $t$ and, consequently, the spin–orbitals $u_i{}^{(0)}(\mathbf{r}_i) + u_i{}^{(1)}(\mathbf{r}_i, t)$, for $i=1$ to $N$, are an orthogonal set. In contrast to the zeroth-order case, there is no self-consistency requirement to be satisfied in Eq. (120), resulting in the designation of this perturbation treatment as the "uncoupled" Hartree–Fock approximation.[68] Similar uncoupled expressions can be written for the second- and higher-order perturbation equations [Eqs. (53)] although we do not reproduce the results here.[69]

## IV. COMPLEMENTARY TREATMENTS OF SECULAR AND NORMALIZATION TERMS

In this section we introduce a simple order-by-order projection procedure that provides an alternative method for isolating the secular and normalization terms in the Dirac perturbation functions and gives further insight into their structure.[21] We consider also a number of additional approaches to the secular divergence problem which have been suggested by workers in the field of nonequilibrium statistical mechanics, as well as in the more classical areas of nonlinear electrical, fluid dynamical, and mechanical systems.[22,23] These methods can be employed to isolate the secular behavior of perturbation solutions to a wide class of linear and nonlinear differential equations, and provide additional physical insight into the source of the secular terms that arise in the perturbation solutions of the time-dependent Schrödinger equation. Finally, we consider the difficulties that can arise due to the presence of secular terms in the Fourier analysis of perturbation approximations to the complete wave function and demonstrate that these difficulties are circumvented by utilization of the regular part of the wave function.

### A. Projection Procedure

We have seen that secular and normalization terms can be extracted from the wave function by factoring out the Dirac coefficient $a_0(t)$, which determines the amplitude for finding the system in the unperturbed state $\Psi^{(0)}(\mathbf{r}, t)$. Since the perturbation equations [Eqs. (19)] are of the linear inhomogeneous type, this suggests that the secular and normalization terms can also be dealt with by means of a procedure which projects out of the time-dependent perturbation equations any contribution to the perturbation functions which is proportional to $\phi_0{}^{(0)}(\mathbf{r})$. We see from

[68] The uncoupled time-dependent Hartree–Fock approximation was first obtained by Karplus and Kolker (1963b) for the case of an harmonic perturbation, and more recently by Heinrichs (1968c), for an arbitrary time-dependent perturbation. Their procedures are slightly different from our own, and, consequently, their resulting orbital equations differ somewhat from Eq. (120). Nevertheless, the functions $\phi_{\mathrm{HF}}{}^{(1)}(\mathbf{r}, t)$ [Eqs. (116) and (117)] obtained from their procedures are identical with our canonical results. To make this clear, we designate the left-hand side of Eq. (120) as $X_i(\mathbf{r}, t)$ and note that Eq. (112) can be written as

$$\sum_{i=1}^{N} \det \mid u_1{}^{(0)}(\mathbf{r}_1)\cdots u_{i-1}{}^{(0)}(\mathbf{r}_{i-1}) X_i(\mathbf{r}_i, t)\, u_{i+1}{}^{(0)}(\mathbf{r}_{i+1})\cdots u_N{}^{(0)}(\mathbf{r}_N) \mid = 0.$$

The general solution of this equation is

$$X_i(\mathbf{r}_i, t) = \sum_{j=1}^{N} \lambda_{ij}(t) u_j{}^{(0)}(\mathbf{r}_i),$$

with the $\lambda_{ij}(t)$ arbitrary for $j \neq i$ but with

$$\sum_{i=1}^{N} \lambda_{ii}(t) = 0.$$

Our Eq. (120) corresponds to the formally simplest choice $\lambda_{ij}(t)=0$ for all $i$ and $j$ whereas Karplus and Kolker, and Heinrichs choose nonzero $\lambda_{ij}(t)$. The solutions of their orbital equations, however, differ from our canonical results only by multiples of the $u_j{}^{(0)}(\mathbf{r}_i)$, which clearly make no contribution to $\phi_{\mathrm{HF}}{}^{(1)}(\mathbf{r}, t)$ of Eqs. (116) and (117) so long as

$$\sum_{i=1}^{N} \lambda_{ii}(t) = 0,$$

a condition satisfied by their choice of $\lambda_{ii}(t)$. In their computational applications, Karplus and Kolker replace the nonlocal Fock operator of Eqs. (109) with a local approximation, thereby simplifying the analysis and eliminating an undesirable feature inherent in the uncoupled Hartree–Fock approximation. This point is discussed in detail by Langhoff, Karplus, and Hurst (1966). Following an alternate derivation, Chung (1967) has derived a set of uncoupled Hartree–Fock perturbation equations which contain spurious coupling terms between first-order orbitals. His result is a consequence of not focusing attention on the regular part of the wave function and thereby including noncontributing secular and spurious normalization terms in the computational procedure. Specifically, the last term on the right-hand side of Eq. (53) in Chung's development gives the spurious coupling terms between first-order orbitals. These terms arise from the third from the last term on the right-hand side of his Eq. (52) which was incorrectly included due to his failure to realize that the first-order perturbed function must be orthogonal to the unperturbed function, from both the normalization requirement and the necessary phase convention discussed in our Footnote 46. Further discussion of this point is given in the variational formulation of Sec. V.C.

[69] The higher-order uncoupled Hartree–Fock equations appropriate for a static single-particle perturbation are discussed by Langhoff (1965).

Eqs. (58) and (59), however, that some of the secular and normalization terms are not proportional to $\phi_0^{(0)}(\mathbf{r})$ and can not be projected out directly this way. Consequently, in the application of the projection technique, it is useful to anticipate the structure of the perturbation functions $\Psi^{(n)}(\mathbf{r}, t)$ as given in Eqs. (58) and (59). When this is done, the nature of the projection procedure is clarified and the development provides additional insight into the structure of the perturbation functions.

We introduce the standard projection operator[70]

$$Q_0 = 1 - |\phi_0^{(0)}\rangle\langle\phi_0^{(0)}| \tag{122}$$

and apply it to the first-order equation [Eq. (19b), $n=1$] in the presence of a general perturbation $H^{(1)}(\mathbf{r}, t)$

$$[H^{(0)}(\mathbf{r}) - i\hbar(\partial/\partial t)]\Psi^{(1)}(\mathbf{r}, t) + H^{(1)}(\mathbf{r}, t)\Psi^{(0)}(\mathbf{r}, t) = 0. \tag{123}$$

Utilizing the fact that $\phi_0^{(0)}(\mathbf{r})$ is an eigenfunction of $H^{(0)}(\mathbf{r})$, we obtain

$$\begin{aligned} Q_0\{[H^{(0)}(\mathbf{r}) - i\hbar(\partial/\partial t)]\Psi^{(1)}(\mathbf{r}, t) + H^{(1)}(\mathbf{r}, t)\Psi^{(0)}(\mathbf{r}, t)\} \\ = [H^{(0)}(\mathbf{r}) - i\hbar(\partial/\partial t)]Q_0\Psi^{(1)}(\mathbf{r}, t) \\ + [H^{(1)}(\mathbf{r}, t) - E^{(1)}(t)]\Psi^{(0)}(\mathbf{r}, t) = 0, \end{aligned} \tag{124}$$

where

$$E^{(1)}(t) = \langle\phi_0^{(0)} | H^{(1)} | \phi_0^{(0)}\rangle. \tag{125}$$

From Eq. (59b) we see that

$$Q_0\Psi^{(1)}(\mathbf{r}, t) = \phi^{(1)}(\mathbf{r}, t)\exp[(i\hbar)^{-1}E_0^{(0)}t], \tag{126}$$

and, consequently, Eq. (124) can be written in the form

$$\begin{aligned} [H^{(0)}(\mathbf{r}) - E_0^{(0)} - i\hbar(\partial/\partial t)]\phi^{(1)}(\mathbf{r}, t) \\ + [H^{(1)}(\mathbf{r}, t) - E^{(1)}(t)]\phi_0^{(0)}(\mathbf{r}) = 0. \end{aligned} \tag{127}$$

From Eqs. (124)–(127) we see that application of the projection procedure to Eq. (123) yields the correct perturbation equation for $\phi^{(1)}(\mathbf{r}, t)$ given in Eq. (53a). To obtain the complete solution $\Psi^{(1)}(\mathbf{r}, t)$, the proper multiple of $\phi_0^{(0)}(\mathbf{r})$ must be added to $\phi^{(1)}(\mathbf{r}, t)$ as in Eq. (59b). In the first-order problem it is a secular term, which does not involve the normalization requirement.[71]

As we have pointed out in Sec. II, the secular terms do not contribute to expectation values. Nevertheless, they must be included in order to obtain the correct higher-order equations, as we shall now demonstrate in the second-order case. Substituting Eq. (59b) for $\Psi^{(1)}(r, t)$ into the second-order equation [Eq. (19b), $n=2$]

$$[H^{(0)}(\mathbf{r}) - i\hbar(\partial/\partial t)]\Psi^{(2)}(\mathbf{r}, t) + H^{(1)}(\mathbf{r}, t)\Psi^{(1)}(\mathbf{r}, t) = 0, \tag{128}$$

gives

$$\begin{aligned} [H^{(0)}(\mathbf{r}) - i\hbar(\partial/\partial t)]\Psi^{(2)}(\mathbf{r}, t) + H^{(1)}(\mathbf{r}, t) \\ \times \left\{\phi^{(1)}(\mathbf{r}, t) + (i\hbar)^{-1}\int_{-\infty}^{t} E^{(1)}(t')\, dt'\phi_0^{(0)}(\mathbf{r})\right\} \\ \times \exp[(i\hbar)^{-1}E_0^{(0)}t] = 0. \end{aligned} \tag{129}$$

In order to investigate the nature of the terms which arise in $\Psi^{(2)}(\mathbf{r}, t)$ due to the presence of the last term on the left-hand side of Eq. (129) (the secular term), we note from Eqs. (123) and (59b) that

$$\begin{aligned} H^{(1)}(\mathbf{r}, t)\Psi^{(0)}(\mathbf{r}, t) &= -[H^{(0)}(\mathbf{r}) - i\hbar(\partial/\partial t)]\Psi^{(1)}(\mathbf{r}, t) \\ &= -\{[H^{(0)}(\mathbf{r}) - E_0^{(0)} - i\hbar(\partial/\partial t)]\phi^{(1)}(\mathbf{r}, t) - E^{(1)}(t)\phi_0^{(0)}(\mathbf{r})\}\exp[(i\hbar)^{-1}E_0^{(0)}t]. \end{aligned} \tag{130}$$

Consequently, using Eq. (130), the last term on the left-hand side of Eq. (129) can be written

$$\begin{aligned} (i\hbar)^{-1}\int_{-\infty}^{t} E^{(1)}(t')\, dt' H^{(1)}(\mathbf{r}, t)\Psi^{(0)}(\mathbf{r}, t) = \left\{-\left(H^{(0)}(\mathbf{r}) - E_0^{(0)} - i\hbar\frac{\partial}{\partial t}\right)\left[(i\hbar)^{-1}\int_{-\infty}^{t} E^{(1)}(t')\, dt'\phi^{(1)}(\mathbf{r}, t)\right.\right. \\ \left.\left. + (i\hbar)^{-2}\left(\int_{-\infty}^{t} E^{(1)}(t')\, dt'\right)^2\phi_0^{(0)}(\mathbf{r})\right] - E^{(1)}(t)\phi^{(1)}(\mathbf{r}, t)\right\}\exp[(i\hbar)^{-1}E_0^{(0)}t]. \end{aligned} \tag{131}$$

Substituting Eq. (131) into Eq. (129) and writing $\Psi^{(2)}(\mathbf{r}, t)$ in the form

$$\Psi^{(2)}(\mathbf{r}, t) = \theta^{(2)}(\mathbf{r}, t)\exp[(i\hbar)^{-1}E_0^{(0)}t], \tag{132}$$

we find

$$\begin{aligned} \left(H^{(0)}(\mathbf{r}) - E_0^{(0)} - i\hbar\frac{\partial}{\partial t}\right)\left[\theta^{(2)}(\mathbf{r}, t) - (i\hbar)^{-1}\int_{-\infty}^{t} E^{(1)}(t')\, dt'\phi^{(1)}(\mathbf{r}, t) - \tfrac{1}{2}(i\hbar)^{-2}\left(\int_{-\infty}^{t} E^{(1)}(t')\, dt'\right)^2\phi_0^{(0)}(\mathbf{r})\right] \\ + [H^{(1)}(\mathbf{r}, t) - E^{(1)}(t)]\phi^{(1)}(\mathbf{r}, t) = 0. \end{aligned} \tag{133}$$

Equations (129) to (133) demonstrate that the secular term in $\Psi^{(1)}(\mathbf{r}, t)$ [Eq. (59b)] gives rise to the last two terms in the large square bracket in Eq. (133) and to the factor $E^{(1)}(t)\phi^{(1)}(\mathbf{r}, t)$, as well. Since this latter factor

[70] See, for example, Messiah (1966) p. 260, and Löwdin (1966) p. 268.

[71] See Footnote 19, p. 1496 of Karplus and Kolker (1963a), which describes the projection operator technique. The statement there that any contribution of $\phi_0^{(0)}(\mathbf{r})$ to $\Psi^{(1)}(\mathbf{r}, t), \Psi^{(2)}(\mathbf{r}, t), \cdots$ can be accounted for by "renormalization" is misleading; the secular terms proportional to $\phi_0^{(0)}(\mathbf{r})$, which do not affect expectation values but are required to obtain the correct higher-order equations, should be included as well.

gives rise to terms in the second-order wave function which contribute to expectation values, it is clear that if the secular term is not included in $\Psi^{(1)}(\mathbf{r}, t)$ in Eq. (129), the correct equations for the second-order functions $\Psi^{(2)}(\mathbf{r}, t)$ and $\phi^{(2)}(\mathbf{r}, t)$ are not obtained.

To complete the development, we project on Eq. (133) with $Q_0$ and obtain

$$\left(H^{(0)}(\mathbf{r})-E_0{}^{(0)}-i\hbar\frac{\partial}{\partial t}\right)\left(Q_0\theta^{(2)}(\mathbf{r}, t)-(i\hbar)^{-1}\int_{-\infty}^{t}E^{(1)}(t')\,dt'\phi^{(1)}(\mathbf{r}, t)\right)+[H^{(1)}(\mathbf{r}, t)-E^{(1)}(t)]\phi^{(1)}(\mathbf{r}, t)$$
$$=E^{(2)}(t)\phi_0{}^{(0)}(\mathbf{r}), \quad (134)$$

where

$$E^{(2)}(t)=\langle\phi_0{}^{(0)}\mid H^{(1)}\mid\phi^{(1)}\rangle. \quad (135)$$

We recognize Eq. (134) as the second-order perturbation equation [Eq. (53b), $n=2$]. Therefore, we have

$$Q_0\theta^{(2)}(\mathbf{r}, t)-(i\hbar)^{-1}\int_{-\infty}^{t}E^{(1)}(t')\,dt'\phi^{(1)}(\mathbf{r}, t)=\phi^{(2)}(\mathbf{r}, t), \quad (136)$$

and from Eq. (132)

$$Q_0\Psi^{(2)}(\mathbf{r}, t)=\left(\phi^{(2)}(\mathbf{r}, t)+(i\hbar)^{-1}\int_{-\infty}^{t}E^{(1)}(t')\,dt'\phi^{(1)}(\mathbf{r}, t)\right)\exp[(i\hbar)^{-1}E_0{}^{(0)}t] \quad (137)$$

in agreement with Eq. (59c).

From Eq. (137) we see that the secular terms in $\Psi^{(2)}(\mathbf{r}, t)$ are not all multiples of the unperturbed wave function $\Psi^{(0)}(\mathbf{r}, t)$. Consequently, the projection procedure when applied to Eq. (128) does not isolate only the regular part of the wave function $\phi^{(2)}(\mathbf{r}, t)$, but also the additional secular term of Eq. (137). That is, projecting with $Q_0$ on Eq. (128) gives

$$[H^{(0)}(\mathbf{r})-i\hbar(\partial/\partial t)]Q_0\Psi^{(2)}(\mathbf{r}, t)+H^{(1)}(\mathbf{r}, t)\Psi^{(1)}(\mathbf{r}, t)-\langle\phi_0{}^{(0)}\mid H^{(1)}\mid\Psi^{(1)}\rangle\phi_0{}^{(0)}(\mathbf{r})=0. \quad (138)$$

In order to isolate the regular function $\phi^{(2)}(\mathbf{r}, t)$, and thereby avoid the possible irregular behavior of a secular term, it is necessary to anticipate the structure of Eq. (137); that is, substituting Eq. (137) for $Q_0\Psi^{(2)}(\mathbf{r}, t)$ into Eq. (138) and Eq. (59b) for $\Psi^{(1)}(\mathbf{r}, t)$ gives

$$[H^{(0)}(\mathbf{r})-E_0{}^{(0)}-i\hbar(\partial/\partial t)]\phi^{(2)}(\mathbf{r}, t)+[H^{(1)}(\mathbf{r}, t)-E^{(1)}(t)]\phi^{(1)}(\mathbf{r}, t)=E^{(2)}(t)\phi_0{}^{(0)}(\mathbf{r}),$$
$$E^{(2)}(t)=\langle\phi_0{}^{(0)}\mid H^{(1)}\mid\phi^{(1)}\rangle, \quad (139)$$

the second-order perturbation equation [Eq. (53b), $n=2$].

It is a simple matter to demonstrate that the projection procedure provides a similar result for the higher-order perturbation equations. Thus, solution of the projections of Eqs. (19) will result in the portions of the $\Psi^{(n)}(\mathbf{r}, t)$ orthogonal to $\phi_0{}^{(0)}(\mathbf{r})$. In order to isolate the regular contribution $\phi^{(n)}(\mathbf{r}, t)$ in each order, it is necessary to anticipate the presence of the secular terms in Eqs. (59) which are orthogonal to $\phi_0{}^{(0)}(\mathbf{r})$, and to substitute the appropriate expressions [e.g., Eq. (137)] into the projected perturbation equations. The resulting equations will then agree with the alternative perturbation equations [Eqs. (53)].

### B. Multiple Time Scales

The procedure we have followed in Sec. II in extracting secular and normalization terms from the time-dependent perturbation functions involved mathematical manipulations performed without consideration of the physical interpretation of the source of secular behavior. To gain some physical understanding of what is involved, it is instructive to consider the multiplicity of time scales in the perturbation problem. In addition to the very fast time scales corresponding to the reciprocals of the unperturbed atomic transition frequencies, the external perturbation (e.g., radiation field) establishes a slower time scale ($\sim 1/\omega$) with which the observed response (e.g., polarization) of the system is associated. This latter time scale may still be fast compared to the very slow time scale corresponding to the reciprocal of the small level shift of the zeroth-order energy induced by the field [Eq. (92)]. The level shift is the physical source of secular divergence, as is evident from the fact that the divergent terms arise from the perturbation expansion of the exponential factor of Eq. (29), as shown in Eqs. (59). Such qualitative considerations suggest that the secular behavior can also be eliminated by a perturbation theory approach that provides for the introduction of a set of conveniently chosen time scales in addition to the fundamental time variable $t$.

A number of formalisms which have been developed to avoid the appearance of secular terms in other disciplines are applicable to the equations of time-dependent perturbation theory. These procedures explicitly introduce an additional set of time scales chosen in a manner designed to eliminate the secular terms. While the utility of the techniques, such as the methods of extension[22] and time averaging,[23] is better exhibited in application to problems in nonequilibrium statistical mechanics and nonlinear dynamics, it is of interest to examine their connection with the development of Sec. II.

To illustrate the use of additional time scales, we consider as an example the equation

$$df(t)/dt = -\lambda f(t); \qquad f(0)=1, \tag{140}$$

with the solution

$$f(t) = \exp(-\lambda t). \tag{141}$$

Introducing the customary perturbation theory expansion

$$f(t) = \sum_{n=0}^{\infty} \lambda^n f^{(n)}(t) \tag{142}$$

into Eq. (140) gives

$$f^{(n)}(t) = (-t)^n/n!. \tag{143}$$

Consequently, Eq. (142) becomes

$$f(t) = \sum_{n=0}^{\infty} \frac{(-\lambda t)^n}{n!} \tag{144}$$

the familiar exponential series. Equation (144) is correct for any $t$ if a sufficient number of terms in the sum are included. If only a finite number are used, however, the expression diverges for large $t$; e.g. for $t \gg 1/\lambda$, the first few terms do not yield a meaningful result. Quite simply, the condition for rapid convergence of Eq. (144) $\lambda t \ll 1$, can always be violated for large $t$ even if $\lambda \ll 1$. We might suspect that the introduction of $\lambda t$ as an additional variable, or time scale, would allow us to avoid this difficulty.

The method of extension when applied to Eq. (140) seeks to avoid the convergence difficulty for large $t$ by considering the extended function $f(t, \lambda t)$, where the variable $\lambda t$ is an additional time scale, in this case a simple multiple of the time. Its introduction is suggested by the fact that $\lambda t \ll 1$ is the condition for rapid convergence of the perturbation solution to Eq. (140), rather than $\lambda \ll 1$. With this, the time derivative takes the form

$$\frac{df(t,\lambda t)}{dt} = \frac{\partial f(t,\lambda t)}{\partial t} + \frac{\partial f(t,\lambda t)}{\partial(\lambda t)} \frac{\partial(\lambda t)}{\partial t}. \tag{145}$$

Introducing this expression and the expansion for $f(t, \lambda t)$

$$f(t,\lambda t) = \sum_{n=0}^{\infty} \lambda^n f^{(n)}(t,\lambda t) \tag{146}$$

into Eq. (140), we have, to first order in $\lambda$,

$$\partial f^{(0)}(t,\lambda t)/\partial t = 0, \tag{147a}$$

$$[\partial f^{(1)}(t,\lambda t)/\partial t] + [\partial f^{(0)}(t,\lambda t)/\partial(\lambda t)] = -f^{(0)}(t,\lambda t). \tag{147b}$$

From Eq. (147a) we see that $f^{(0)}(t, \lambda t)$ is independent of $t$, but not necessarily of $\lambda t [f^{(0)}(t,\lambda t) \to f^{(0)}(\lambda t)]$. Consequently, integration of Eq. (147b) with respect to $t$ yields

$$f^{(1)}(t,\lambda t) = -t\{f^{(0)}(\lambda t) + [\partial f^{(0)}(\lambda t)/\partial(\lambda t)]\} + h(\lambda t), \tag{148}$$

where $h(\lambda t)$ is an integration constant with respect to the $t$ integration. The function $f^{(1)}(t, \lambda t)$ evidently diverges with $t$, as in Eq. (144), unless $f^{(0)}(\lambda t)$ is required to depend on $\lambda t$ such that

$$\partial f^{(0)}(\lambda t)/\partial(\lambda t) = -f^{(0)}(\lambda t), \tag{149a}$$

or

$$f^{(0)}(\lambda t) = \exp(-\lambda t). \tag{149b}$$

We see that extending the function $f(t)$ by introducing the additional variable $\lambda t$, together with the condition Eqs. (149) sums the perturbation expansion of Eq. (142) so that the exact solution is obtained. Thus the integration constant $h(\lambda t)$ in Eq. (148) can be set equal to zero. The similarity of this simple example to the equations of time-dependent perturbation theory for a static perturbation, where secular divergences result from the expansion of an exponential factor [Eq. (26)], is evident.

As a second example of the use of additional time scales, we consider the more general equation

$$df(t)/dt = -\lambda g(t) f(t); \qquad f(0)=1, \tag{150}$$

where $g(t)$ is an arbitrary function of the time. The solution of Eq. (150) is ($t \geq 0$)

$$f(t) = \exp\left(-\lambda \int_0^t g(t')\, dt'\right), \tag{151}$$

and convergence difficulties for large $t$ corresponding to those obtained from Eq. (144) can result from the perturbation expansion of Eq. (151). We can avoid this problem by introducing the additional time scale $\lambda\tau(t)$, which is at this point an arbitrary function of $t$, and the extended function $f(t, \lambda\tau)$. The time derivative now takes the form

$$\frac{df(t,\lambda\tau)}{dt} = \frac{\partial f(t,\lambda\tau)}{\partial t} + \lambda \frac{\partial f(t,\lambda\tau)}{\partial(\lambda\tau)} \frac{\partial\tau(t)}{\partial t}. \tag{152}$$

Employing this expression and the expansion of $f(t, \lambda\tau)$ itself [corresponding to that in Eq. (146)] in Eq. (150), we obtain in first order

$$\partial f^{(0)}(t,\lambda\tau)/\partial t = 0, \tag{153a}$$

$$\frac{\partial f^{(1)}(t,\lambda\tau)}{\partial t} + \frac{\partial f^{(0)}(t,\lambda\tau)}{\partial(\lambda\tau)} \frac{\partial\tau(t)}{\partial t} = -g(t) f^{(0)}(t,\lambda\tau), \tag{153b}$$

equations similar to Eqs. (147). Integrating Eq. (153b) with respect to $t$, we find

$$f^{(1)}(t,\lambda\tau) = -f^{(0)}(\lambda\tau) \int_0^t g(t')\, dt' - \frac{\partial f^{(0)}(\lambda\tau)}{\partial(\lambda\tau)} \int_0^t \frac{\partial\tau(t')}{\partial t'}\, dt', \tag{154}$$

where we have made use of the fact that $f^{(0)}(\lambda\tau)$ is independent of $t$ [Eq. (153a)]. In order to avoid the possible divergent behavior of $f^{(1)}(t, \lambda\tau)$ for large $t$, we choose the arbitrary time scale $\lambda\tau(t)$ so that it follows

the time integrated behavior of $g(t)$ (time averaging); i.e.,

$$\partial\tau(t)/\partial t = g(t), \tag{155a}$$

or

$$\tau(t) = \int_0^t g(t')\, dt'. \tag{155b}$$

Using this result in Eq. (154), we see that we can eliminate the $t$ dependence of $f^{(1)}(t, \lambda\tau)$ entirely by demanding that $f^{(0)}(\lambda\tau)$ depend on $\lambda\tau(t)$, such that

$$\partial f^{(0)}(\lambda\tau)/\partial(\lambda\tau) = -f^{(0)}(\lambda\tau), \tag{156a}$$

or

$$f^{(0)}(\lambda\tau) = \exp\left(-\lambda\int_0^t g(t')\, dt'\right) \tag{156b}$$

from Eq. (155b). The single additional time scale, Eqs. (155), is evidently sufficient to obtain the exact solution in this case.

In both of the preceding simple examples, which correspond to Eq. (28a) for static and time-dependent perturbations, respectively, the introduction of additional time scales was a trivial exercise. The original equations in both cases were simply integrable and, therefore, it is not surprising that the introduction of a single additional time scale in the perturbation expansion allowed summation of the entire series.

We can apply the methods of additional time scales to the perturbation sequence of Eq. (19) by considering the extended wave function $\Psi(\mathbf{r}, t, \tau_1, \tau_2, \cdots)$, in terms of which the Schrödinger equation becomes[72,73]

$$[H^{(0)}(\mathbf{r}) + H^{(1)}(\mathbf{r}, t) - i\hbar(d/dt)]\Psi(\mathbf{r}, t, \tau_1, \tau_2, \cdots) = 0, \tag{157}$$

where we have written a total time derivative to emphasize the implicit time dependence of the wave function on $t$ through the functions $\tau_1(t)$, $\tau_2(t)$, $\cdots$. To illustrate the method, we determine the wave function to first order, and introduce the single additional time scale $\tau(t)$, which we assume to be first-order in the perturbation parameter, in analogy with the illustrative examples. In Eq. (157) we now have

$$[d\Psi(\mathbf{r}, t, \tau)/dt] = [\partial\Psi(\mathbf{r}, t, \tau)/\partial t] + [\partial\Psi(\mathbf{r}, t, \tau)/\partial\tau][\partial\tau(t)/\partial t], \tag{158}$$

and introducing the perturbation expansion

$$\Psi(\mathbf{r}, t, \tau) = \Psi^{(0)}(\mathbf{r}, t, \tau) + \Psi^{(1)}(\mathbf{r}, t, \tau) + \cdots, \tag{159}$$

Eq. (157) gives to first order,

$$[H^{(0)}(\mathbf{r}) - i\hbar(\partial/\partial t)]\Psi^{(0)}(\mathbf{r}, t, \tau) = 0, \tag{160a}$$

$$[H^{(0)}(\mathbf{r}) - i\hbar(\partial/\partial t)]\Psi^{(1)}(\mathbf{r}, t, \tau) + H^{(1)}(\mathbf{r}, t)\Psi^{(0)}(\mathbf{r}, t, \tau) - i\hbar[\partial\Psi^{(0)}(\mathbf{r}, t, \tau)/\partial\tau][\partial\tau(t)/\partial t] = 0. \tag{160b}$$

[72] Our subsequent discussion closely follows that of Case (1966).

[73] Corresponding applications of multiple-time-scales perturbation theory to the Schrödinger equation are given by Brooks and Scarfone (1969), in the transition case and by Orr and Ward (1971), in the dispersion case.

The general solution of Eq. (160a) is

$$\Psi^{(0)}(\mathbf{r}, t, \tau) = b^{(0)}(\tau)\phi_0^{(0)}(\mathbf{r}) \exp[(i\hbar)^{-1}E_0^{(0)}t], \tag{161}$$

where the integration "constant" $b^{(0)}(\tau)$ is an arbitrary function of $\tau(t)$. Introducing for convenience the function $\theta^{(1)}(\mathbf{r}, t, \tau)$ of the form

$$\Psi^{(1)}(\mathbf{r}, t, \tau) = \theta^{(1)}(\mathbf{r}, t, \tau) \exp[(i\hbar)^{-1}E_0^{(0)}t], \tag{162}$$

and substituting this and Eq. (161) into Eq. (160b), we obtain

$$[H^{(0)}(\mathbf{r}) - E_0^{(0)} - i\hbar(\partial/\partial t)]\theta^{(1)}(\mathbf{r}, t, \tau) + H^{(1)}(\mathbf{r}, t)b^{(0)}(\tau)\phi_0^{(0)}(\mathbf{r}) - i\hbar[\partial b^{(0)}(\tau)/\partial\tau]\phi_0^{(0)}(\mathbf{r})[\partial\tau(t)/\partial t] = 0. \tag{163}$$

We now choose $\tau(t)$ and $b^{(0)}(\tau)$ so that the possible secular behavior of $\theta^{(1)}(\mathbf{r}, t, \tau)$ is avoided. To make this clear, we introduce the spectral expansion

$$\theta^{(1)}(\mathbf{r}, t, \tau) = \sum_{k=0}^{\infty} a_k^{(1)}(t, \tau)\phi_k^{(0)}(\mathbf{r}) \times \exp[(i\hbar)^{-1}(E_k^{(0)} - E_0^{(0)})t] \tag{164}$$

into Eq. (163) and find

$$a_k^{(1)}(t, \tau) = (i\hbar)^{-1}b^{(0)}(\tau)\int_{-\infty}^{t} \langle\phi_k^{(0)} \mid H^{(1)} \mid \phi_0^{(0)}\rangle \times \exp[(i\hbar)^{-1}(E_0^{(0)} - E_k^{(0)})t']\, dt' \qquad k \neq 0, \tag{165a}$$

$$a_0^{(1)}(t, \tau) = (i\hbar)^{-1}b^{(0)}(\tau)\int_{-\infty}^{t} \langle\phi_0^{(0)} \mid H^{(1)} \mid \phi_0^{(0)}\rangle\, dt' - \frac{\partial b^{(0)}(\tau)}{\partial\tau}\int_{-\infty}^{t}\frac{\partial\tau(t')}{\partial t'}\, dt'. \tag{165b}$$

The particular exponential factors appearing in Eq. (164) are introduced in order to simplify the resulting Eqs. (165). From Eqs. (164) and (165) we see that there is a possibility of $\theta^{(1)}(\mathbf{r}, t, \tau)$ becoming unbounded with $t \to +\infty$ due to the $k = 0$ term, since there are no exponential factors in the integrals of Eq. (165b). This possibility can be avoided by choosing $b^{(0)}(\tau)$ and $\tau(t)$ in Eq. (165b) so that $a_0^{(1)}(t, \tau)$ vanishes for all $t$, similar to the development of Eqs. (150)–(156). The requirements

$$\partial\tau(t)/\partial t = \langle\phi_0^{(0)} \mid H^{(1)} \mid \phi_0^{(0)}\rangle = E^{(1)}(t), \tag{166a}$$

$$\partial b^{(0)}(\tau)/\partial\tau = (i\hbar)^{-1}b^{(0)}(\tau), \tag{166b}$$

will insure that $a_0^{(1)}(t, \tau) = 0$. Equations (166) are sufficient to determine both $\tau(t)$ and $b^{(0)}(\tau)$ and we find that

$$\tau(t) = \int_{-\infty}^{t} E^{(1)}(t')\, dt' \tag{167a}$$

$$b^{(0)}(\tau) = \exp\left((i\hbar)^{-1}\int_{-\infty}^{t} E^{(1)}(t')\, dt'\right). \tag{167b}$$

Inserting these results into Eq. (163) and noting that

we can write $\theta^{(1)}(\mathbf{r}, t, \tau)$ in the form [Eqs. (164) and (165a)]

$$\theta^{(1)}(\mathbf{r}, t, \tau) = b^{(0)}(\tau)\phi^{(1)}(\mathbf{r}, t), \tag{168}$$

we obtain

$$[H^{(0)}(\mathbf{r}) - E_0^{(0)} - i\hbar(\partial/\partial t)]\phi^{(1)}(\mathbf{r}, t) + [H^{(1)}(\mathbf{r}, t) - E^{(1)}(t)]\phi^{(0)}(\mathbf{r}) = 0. \tag{169}$$

Consequently, the wave function through first-order [Eq. (159)] is

$$\Psi(\mathbf{r}, t, \tau) = [\phi_0^{(0)}(\mathbf{r}) + \phi^{(1)}(\mathbf{r}, t) + \cdots] \times \exp\left[(i\hbar)^{-1}\left(E_0^{(0)}t + \int_{-\infty}^{t} E^{(1)}(t')\, dt' + \cdots\right)\right]. \tag{170}$$

Thus, we see that the requirements of Eqs. (166), which insure that the wave function is bounded in $t$, lead to the correct first-order perturbation equation [Eq. (169)] and the correct first-order phase factor in the over-all wave function [Eq. (170)].

The foregoing procedure can also be applied to the higher-order time-dependent perturbation equations to reproduce the results of Sec. II. Some care must be exercised, however, in the second- and higher-order cases due to the presence of both secular and normalization terms in the perturbation functions. By contrast, the procedure of Sec. II explicitly isolates both secular and normalization terms in the wave function to all orders in perturbation theory and thus appears to obviate the need for application of the method of additional time scales to the Schrödinger equation.

### C. Fourier Analysis

In the case of a general time-dependent perturbation, Fourier analysis can be useful in obtaining solutions to the Schrödinger equation.[74] The alternative time-dependent equation [Eq. (28b)], and the associated perturbation expansion [Eq. (53)], exhibit advantages in this regard over the original Schrödinger equation. In Eq. (1)

$$[H^{(0)}(\mathbf{r}) - i\hbar(\partial/\partial t)]\Psi(\mathbf{r}, t) + H^{(1)}(\mathbf{r}, t)\Psi(\mathbf{r}, t) = 0, \tag{171}$$

we are concerned with the Fourier analysis of the term

$$H^{(1)}(\mathbf{r}, t)\Psi(\mathbf{r}, t) = (2\pi)^{-1/2}\int_{-\infty}^{+\infty} K(\mathbf{r}, \omega)\exp(-i\omega t)\, d\omega, \tag{172}$$

or its perturbation expansion. It is clear that the Fourier transform

$$K(\mathbf{r}, \omega) = (2\pi)^{-1/2}\int_{-\infty}^{+\infty} H^{(1)}(\mathbf{r}, t)\Psi(\mathbf{r}, t)\exp(i\omega t)\, dt \tag{173}$$

will not exist if the integral

$$I = \lim_{T\to\infty}\int_{-T}^{+T} H^{(1)}(\mathbf{r}, t)\Psi(\mathbf{r}, t)\, dt \tag{174}$$

diverges.[75] One possible cause for a divergence in Eq. (174) in a physically well-defined problem is the presence of secular divergent terms in $\Psi(\mathbf{r}, t)$. By contrast, in the Fourier analysis of the corresponding term of Eq. (28b),

$$[H^{(0)}(\mathbf{r}) - E_0^{(0)} - i\hbar(\partial/\partial t)]\phi(\mathbf{r}, t) + [H^{(1)}(\mathbf{r}, t) - \Delta E(t)]\phi(\mathbf{r}, t) = 0, \tag{175}$$

we recognize that the Fourier transform

$$G(\mathbf{r}, \omega) = (2\pi)^{-1/2}\int_{-\infty}^{+\infty}[H^{(1)}(\mathbf{r}, t) - \Delta E(t)]\phi(\mathbf{r}, t) \times \exp(i\omega t)\, dt, \tag{176}$$

or its perturbation expansion, cannot be ill-defined due to secular terms, since they do not appear in $\phi(\mathbf{r}, t)$. Consequently, the extraction of the secular terms from the time-dependent wave function assures that the Fourier analysis of Eq. (175) may be possible even when a similar procedure is not valid in Eq. (171).

## V. VARIATIONAL FORMULATION

In this section we employ the Frenkel variational principle and a trial wave function in the form of Eq. (33) to obtain a computationally convenient variational principle that provides a bound to the system level shift induced by a periodic perturbation. This form of the Frenkel principle is a unification of the second- and higher-order variational formulations described previously,[7] and yields the familiar Ritz principle in the static limit. We also apply the general development to determine the variational forms of the uncoupled and coupled Hartree–Fock approximations to time-dependent perturbation theory.

### A. Unified Variational Formulation

Variational principles for the perturbation functions of Eqs. (88) have been described previously in the literature and shown to be suitable for computational applications. Although such an order-by-order procedure can give correct results, it is instructive to develop a unified approach which does not depend on a perturbation expansion. As we shall show, a bounded variational formulation can be obtained from the well-known Frenkel variational principle when the trial wave function employed is written in a form similar to Eq. (33), where the secular and normalization terms are extracted to all orders.

The time-dependent variational principle given by Frenkel is[18]

$$\langle\delta\tilde{\Psi}\,|\,H^{(0)} + H^{(1)} - i\hbar(\partial/\partial t)\,|\,\tilde{\Psi}\rangle = 0, \tag{177}$$

[74] See, for example, Morse and Feshbach (1953) Chap. 4, Sec. 8, and Karplus and Kolker (1963a).

[75] See, for example, Franklin (1949) p. 92.

where $\tilde{\Psi}(\mathbf{r},t)$ is an approximate solution of Eq. (1), and $\delta\tilde{\Psi}(\mathbf{r},t)$ is an arbitrary variation about $\tilde{\Psi}(\mathbf{r},t)$. The validity of the Frenkel principle is, of course, not restricted to the perturbation case of interest here but applies to an arbitrary time-dependent Hermitian Hamiltonian. Equation (177) is not in the form of the variation of a functional set equal to zero. Consequently, unlike the Ritz variation principle, which can provide a bound to the total energy in the static case, the Frenkel variational principle of Eq. (177) appears not to furnish a bound to a property of physical interest. A variational procedure which does furnish such a bound, especially on the response of a system to an external perturbation, would be highly desirable.[76] The existence of a bounded variational principle is suggested by previously described order-by-order variational procedures, which can provide bounds to optical susceptibilities in the case of an electromagnetic perturbation.[7,8]

To investigate the possibility of obtaining a bound from the Frenkel principle, we add Eq. (177) to its complex conjugate and obtain

$$\delta\langle\tilde{\Psi}\mid H^{(0)}+H^{(1)}-i\hbar(\partial/\partial t)\mid\tilde{\Psi}\rangle+i\hbar(\partial/\partial t)\langle\tilde{\Psi}\mid\delta\tilde{\Psi}\rangle=0. \tag{178}$$

This form of the Frenkel principle is perfectly general and provides the correct solution of the Schrödinger equation if a sufficiently flexible trial function is employed.[77] We recall from the development of Sec. II.B that the correct solution of the Schrödinger equation can be expressed entirely in terms of the regular function $\phi(\mathbf{r},t)$ of Eq. (33). It is also possible to deal explicitly with the regular portion $\tilde{\phi}(\mathbf{r},t)$ of any approximate trial function $\tilde{\Psi}(\mathbf{r},t)$ employed in the Frenkel principle [Eq. (178)]. This is particularly important for an harmonic perturbation, in which case the regular function is periodic, $\phi(\mathbf{r},t+\tau)=\phi(\mathbf{r},t)$, but the over-all wave function is only quasiperiodic [Eq. (45)],[39] and satisfies the "Bloch condition"

$$\Psi(\mathbf{r},t+\tau)=\Psi(\mathbf{r},t)\exp[(i\hbar)^{-1}(E_0^{(0)}+\Delta E)\tau]. \tag{179}$$

As we shall see, for wave functions satisfying Eq. (179), a time average over one period of Eq. (178) will provide a variational principle for the level shift $\Delta E$.

[76] A time-dependent minimum principle has been discussed by McLachlan (1964). However, the bounded quantity in his approach is not a property of physical interest and, in fact, vanishes for the correct wave function.

[77] The Frenkel principle is sometimes written in the form of Eq. (178) but with the second term on the left-hand side missing. This form of the principle is generally incorrect, since carrying out the indicated variation does not result in the Schrödinger equation and its complex conjugate; i.e., $-i\hbar(\partial/\partial t)$ is not an Hermitian operator in the Hilbert space of $H^{(0)}(\mathbf{r})$, and the second term on the left-hand side of Eq. (178) is required in order to recover the Schrödinger equation and its complex conjugate from the Frenkel principle. While in certain special cases, it is possible to write an arbitrary variation $\delta\tilde{\Psi}(\mathbf{r},t)$ of a trial function $\tilde{\Psi}(\mathbf{r},t)$ in such a form that $(\partial/\partial t)\langle\tilde{\Psi}\mid\delta\tilde{\Psi}\rangle\equiv 0$, it is nevertheless formally incorrect to neglect the second term on the left-hand side of Eq. (178). A restricted form of Frenkel's principle, which requires that $\langle\tilde{\Psi}\mid\delta\tilde{\Psi}\rangle=0$ and $\langle\tilde{\Psi}\mid H-i\hbar(\partial/\partial t)\mid\tilde{\Psi}\rangle=0$, has been discussed recently by Löwdin and Mukherjee (1972).

In order to isolate the secular and normalization terms in the over-all trial wave function, we introduce the ansatz

$$\tilde{\Psi}(\mathbf{r},t)=\tilde{\phi}(\mathbf{r},t)\exp\left[(i\hbar)^{-1}\int_{-\infty}^{t}K[\tilde{\phi}]\,dt'\right], \tag{180}$$

where the functional $K[\tilde{\phi}]$ in Eq. (180) is given by

$$K[\tilde{\phi}]=\langle\tilde{\phi}\mid H^{(0)}+H^{(1)}-i\hbar(\partial/\partial t)\mid\tilde{\phi}\rangle\langle\tilde{\phi}\mid\tilde{\phi}\rangle^{-1}, \tag{181}$$

and $\tilde{\phi}(\mathbf{r},t)$ is a trial function satisfying the constraint

$$\langle\tilde{\phi}\mid\phi_0^{(0)}\rangle=1. \tag{182}$$

This particular form for $K[\tilde{\phi}]$ is suggested by Eq. (28d)

$$E^{(0)}+\Delta E(t)=\langle\phi\mid H^{(0)}+H^{(1)}-i\hbar(\partial/\partial t)\mid\phi\rangle\langle\phi\mid\phi\rangle^{-1}, \tag{183}$$

since at the solution point $\tilde{\phi}(\mathbf{r},t)=\phi(\mathbf{r},t)$ we have

$$K[\phi]=E^{(0)}+\Delta E(t), \tag{184}$$

and Eq. (180) becomes the correct wave function written in the form of Eq. (33). Inserting the general ansatz of Eq. (180) into the Frenkel principle [Eq. (178)], we obtain

$$\delta K[\tilde{\phi}]+i\hbar(\partial/\partial t)(\langle\tilde{\phi}\mid\delta\tilde{\phi}\rangle\langle\tilde{\phi}\mid\tilde{\phi}\rangle^{-1})=0. \tag{185}$$

Carrying out the indicated variation in Eq. (185) and incorporating the normalization requirement of Eq. (182) gives the correct differential equation for $\phi(r,t)$ [Eqs. (28)] when a completely flexible trial function $\tilde{\phi}(\mathbf{r},t)$ is employed. The functional $K[\tilde{\phi}]$ is generally complex; separating it into its real and imaginary parts

$$K[\tilde{\phi}]=\mathrm{Re}\,K[\tilde{\phi}]+i\,\mathrm{Im}\,K[\tilde{\phi}], \tag{186}$$

we have

$$\mathrm{Re}\,K[\tilde{\phi}]=\langle\tilde{\phi}\mid H^{(0)}+H^{(1)}\mid\tilde{\phi}\rangle\langle\tilde{\phi}\mid\tilde{\phi}\rangle^{-1}-(i\hbar/2)(\langle\tilde{\phi}\mid(\partial\tilde{\phi}/\partial t)\rangle-\langle(\partial\tilde{\phi}/\partial t)\mid\tilde{\phi}\rangle)\langle\tilde{\phi}\mid\tilde{\phi}\rangle^{-1} \tag{187a}$$

$$\mathrm{Im}\,K[\tilde{\phi}]=-(\hbar/2)(\langle\tilde{\phi}\mid(\partial\tilde{\phi}/\partial t)\rangle+\langle(\partial\tilde{\phi}/\partial t)\mid\tilde{\phi}\rangle)\langle\tilde{\phi}\mid\tilde{\phi}\rangle^{-1}=-(\hbar/2)(\partial/\partial t)(\ln\langle\tilde{\phi}\mid\tilde{\phi}\rangle). \tag{187b}$$

Consequently, Eq. (185) becomes

$$\begin{aligned}&\delta\,\mathrm{Re}\,K[\tilde{\phi}]+i\delta\,\mathrm{Im}\,K[\tilde{\phi}]+i\hbar(\partial/\partial t)(\langle\tilde{\phi}\mid\delta\tilde{\phi}\rangle\langle\tilde{\phi}\mid\tilde{\phi}\rangle^{-1})\\&=\delta\,\mathrm{Re}\,K[\tilde{\phi}]+i\hbar(\partial/\partial t)(\langle\tilde{\phi}\mid\delta\tilde{\phi}\rangle\langle\tilde{\phi}\mid\tilde{\phi}\rangle^{-1}-\tfrac{1}{2}\delta\ln\langle\tilde{\phi}\mid\tilde{\phi}\rangle)\\&=\delta\,\mathrm{Re}\,K[\tilde{\phi}]+(i\hbar/2)(\partial/\partial t)[(\langle\tilde{\phi}\mid\delta\tilde{\phi}\rangle-\langle\delta\tilde{\phi}\mid\tilde{\phi}\rangle)\langle\tilde{\phi}\mid\tilde{\phi}\rangle^{-1}]=0.\end{aligned} \tag{188}$$

In contrast to the original form of the Frenkel principle [Eq. (178)], the secular and normalization terms do not appear in the variational principle of Eqs. (185) and (188).

The development of Eqs. (180)–(188) is clearly valid for an arbitrary time-dependent Hamiltonian. In the special case of a simple harmonic perturbation,[78] or for the individual Fourier components of a general perturbation, for which a periodic trial function

$$\tilde{\phi}(\mathbf{r}, t+\tau) = \tilde{\phi}(\mathbf{r}, t) \tag{189}$$

is appropriate, a time average of Eq. (188) over one period will eliminate the time derivative appearing there. Carrying out the time average over one period in Eq. (188) gives the desired form of the Frenkel variational principle

$$\delta\{\mathrm{Re}\, K[\tilde{\phi}]\} = 0 \tag{190a}$$

where the bracket $\{\ \}$ designates

$$\{\mathrm{Re}\, K[\tilde{\phi}]\} \equiv (1/\tau) \int_t^{t+\tau} \mathrm{Re}\, K[\tilde{\phi}]\, dt' \tag{190b}$$

as in Eq. (49). At the solution point $\tilde{\phi}(\mathbf{r}, t) = \phi(\mathbf{r}, t)$, we have [Eq. (49)]

$$\{\mathrm{Re}\, K[\phi]\} = \{\mathrm{Re}\, \Delta E(t)\} \equiv \Delta E \tag{190c}$$

and, consequently, we identify Eq. (190a) as a variational principle appropriate for the physical level shift of the system. As we shall show below, Eq. (190a) provides a bound to the system level shift [Eq. (190c)] and a unification of previously described order-by-order variational formulations.

It is also instructive to express the Frenkel principle in terms of a trial function similar to $\chi(\mathbf{r}, t)$ of Eq. (36). Introducing

$$\tilde{\chi}(\mathbf{r}, t) = \tilde{\phi}(\mathbf{r}, t) \langle \tilde{\phi} \mid \tilde{\phi} \rangle^{-1/2}, \tag{191}$$

and Eq. (187b) in the form

$$\exp\left[(\hbar)^{-1} \int_{-\infty}^{t} \mathrm{Im}\, K[\tilde{\phi}]\, dt'\right] = \langle \tilde{\phi} \mid \tilde{\phi} \rangle^{-1/2}, \tag{192}$$

into the ansatz of Eq. (180), we obtain

$$\tilde{\Psi}(\mathbf{r}, t) = \tilde{\chi}(\mathbf{r}, t) \exp\left[(i\hbar)^{-1} \int_{-\infty}^{t} J[\tilde{\chi}]\, dt'\right], \tag{193a}$$

where [Eq. (191)]

$$\langle \tilde{\chi} \mid \tilde{\chi} \rangle = 1, \tag{193b}$$

and

$$J[\tilde{\chi}] \equiv \langle \tilde{\chi} \mid H^{(0)} + H^{(1)} - i\hbar(\partial/\partial t) \mid \tilde{\chi} \rangle = \mathrm{Re}\, K[\tilde{\phi}]. \tag{194}$$

Inserting Eq. (193a) into Eq. (178) gives the variational principle

$$\delta J[\tilde{\chi}] + i\hbar(\partial/\partial t) \langle \tilde{\chi} \mid \delta\tilde{\chi} \rangle = 0. \tag{195}$$

Carrying out the indicated variation in Eq. (195) and incorporating the normalization requirement of Eq. (193b) gives the correct differential equation for $\chi(\mathbf{r}, t)$ [Eqs. (41)] when a completely flexible trial function $\tilde{\chi}(\mathbf{r}, t)$ is employed. In the case of a simple harmonic perturbation, for which the trial function $\tilde{\chi}(r, t)$ satisfies

$$\tilde{\chi}(\mathbf{r}, t+\tau) = \tilde{\chi}(\mathbf{r}, t), \tag{196}$$

we employ a time average over one period in Eq. (195) and obtain

$$\delta\{J[\tilde{\chi}]\} = 0. \tag{197}$$

This result is clearly equivalent to Eqs. (190) [see Eq. (194)], where we employ the variational function $\tilde{\phi}(\mathbf{r}, t)$.

The variational principle of Eq. (197) has been described previously in the literature without making reference to its connection with the Frenkel principle.[15] The implementation of Eq. (197) requires the trial function $\tilde{\chi}(\mathbf{r}, t)$ to satisfy an explicit normalization condition [Eq. (193b)], which can be accomplished by using the Lagrangian multiplier method or by choosing $\tilde{\chi}(\mathbf{r}, t)$ in the form of Eq. (191). The latter choice results in the variational principle given by Eqs. (190). The trial function $\tilde{\phi}(\mathbf{r}, t)$ appearing there must be constrained to be the sum of the unperturbed function $\phi_0^{(0)}(\mathbf{r})$ and an orthogonal complement [Eq. (182)], which can be accomplished also by use of Lagrangian multipliers. We recognize that, by contrast, the Frenkel variational principle in its original form [Eq. (178)] does not require an explicit normalization constraint. That is, although the variation $\delta\tilde{\Psi}(\mathbf{r}, t)$ in Eq. (178) can be carried out subject to a normalization constraint [Eq. (4)], the Lagrangian multiplier introduced in the customary manner to satisfy this demand can be set equal to zero, since the Hermiticity of the Hamiltonian and the resulting time-dependent Schrödinger equation itself will insure that the correct solution has a constant norm. Carrying out the indicated variations in Eqs. (190) and (197), however, does not result in the correct solution of the Schrödinger equation [Eqs. (28) and (41)] unless the normalization requirements [Eqs. (23) and (37)] are explicitly enforced. These requirements arise because the forms of the functionals of Eqs. (190) and (197) have been obtained subject to the conditions of Eqs. (182) and (193b).

To determine the conditions under which the time-averaged functional of Eqs. (190) and (197) provides a bound to the system level shift, we employ the complete orthonormal set of solutions $\chi_k(\mathbf{r}, t)$ of Eqs. (41) for an

[78] Variational principles for the time-dependent Schrödinger equation are generally designed to determine the time dependence of the wave function, as well as the spatial dependence. This is emphasized, for example, in the approach of McLachlan (1964), by his use of the variational function $\theta(\mathbf{r}, t) = i\hbar[\partial\tilde{\Psi}(\mathbf{r}, t)/\partial t]$, which satisfies $\theta(\mathbf{r}, t) = H(\mathbf{r}, t)\Psi(\mathbf{r}, t)$ at the solution point. By contrast, we are here interested primarily in the spatial portion of the wave function and specialize to the case of an harmonic perturbation. Since the harmonic case is of considerable interest in itself, due to its central role in the interactions of radiation and matter, and in view of the general possibility of Fourier analyzing an arbitrary time-dependent perturbation (Sec. IV.C), this specialization is not a stringent limitation.

adiabatically switched periodic perturbation,[79] and introduce the expansion

$$\tilde{\chi}(\mathbf{r}, t) = \sum_{k=0}^{\infty} \tilde{a}_k \chi_k(\mathbf{r}, t), \tag{198a}$$

where the $\tilde{a}_k$ are time-independent variational coefficients which satisfy the normalization condition [Eq. (193b)]

$$\sum_{k=0}^{\infty} | \tilde{a}_k |^2 = 1. \tag{198b}$$

Substituting Eq. (198a) into the functional of Eqs. (190b) and (194), we find

$$\{J[\tilde{\chi}]\} = \sum_{k=0}^{\infty} | \tilde{a}_k |^2 (E_k^{(0)} + \Delta E_k), \tag{199}$$

where $\Delta E_k$ is the level shift associated with the periodic function $\chi_k(\mathbf{r}, t)$. It is clear from Eqs. (198) and (199) that when the level shift of the ground state of the system satisfies $\Delta E \leq \Delta E_k$ for all $k$, then

$$\{J[\tilde{\chi}]\} \geq \{J[\chi]\} = E_0^{(0)} + \Delta E \tag{200}$$

and a bounded variational principle obtains. However, it is important to recognize that Eq. (200) is appropriate for the ground state of the system only when the applied frequency $\omega$ is chosen to insure that transitions into excited states cannot occur.[80]

In the case of an adiabatically switched-on static perturbation we have seen that the wave function takes the form of Eq. (77). To determine the static limit of our variational principle, we let $(t \to +\infty)$ and $\tilde{\phi}(\mathbf{r}, t) \to \tilde{\phi}_s(\mathbf{r})$. The time integration in Eqs. (190) factors out in this case, resulting in

$$\delta \operatorname{Re} K_s[\tilde{\phi}_s] = \delta(\langle \tilde{\phi}_s \mid H^{(0)} + H_s^{(1)} \mid \tilde{\phi}_s \rangle \langle \tilde{\phi}_s \mid \tilde{\phi}_s \rangle^{-1}) = 0, \tag{201}$$

the Ritz principle for the total energy. For the ground state of a system, we obtain the familiar result

$$\operatorname{Re} K_s[\tilde{\phi}_s] \geq \operatorname{Re} K_s[\phi_s] = E_0^{(0)} + \Delta E_s, \tag{202}$$

from Eq. (200), where $\phi_s(\mathbf{r})$ is the solution of the time-independent Schrödinger equation and $\Delta E_s$ the associated static level shift.

### B. Variation-Perturbation Theory

To demonstrate that the variational principle of Eqs. (190) and (197) provides a unification of the previously given order-by-order variational formulations in the case of an harmonic perturbation, we proceed sequentially and first write the trial wave function in the form

$$\tilde{\phi}(\mathbf{r}, t) = \phi_0^{(0)}(\mathbf{r}) + \tilde{\phi}^{(1)}(\mathbf{r}, t) + \cdots, \tag{203}$$

where $\phi_0^{(0)}(\mathbf{r})$ is the unperturbed solution and $\tilde{\phi}^{(1)}(\mathbf{r}, t)$ is a trial perturbation solution which is orthogonal to $\phi_0^{(0)}(\mathbf{r})$. That is, the variation of $\tilde{\phi}^{(1)}(\mathbf{r}, t)$ must be consistent with the orthogonality condition [Eq. (182)]. From Eq. (87a) we see that the trial function $\tilde{\phi}^{(1)}(\mathbf{r}, t)$ for the harmonic perturbation of Eq. (80) can be written in the form $(t \to +\infty)$

$$\tilde{\phi}^{(1)}(\mathbf{r}, t) = \tilde{\phi}_{+1}^{(1)}(\mathbf{r}) \exp(i\omega t) + \tilde{\phi}_{-1}^{(1)}(\mathbf{r}) \exp(-i\omega t). \tag{204}$$

Substituting Eqs. (203) and (204) into $\{\operatorname{Re} K[\tilde{\phi}]\}$ [Eq. (187a)] and retaining terms through second-order, we find for the perturbation of Eq. (80) $(t \to +\infty)$[81]

$$\{\operatorname{Re} K[\tilde{\phi}]\} = E_0^{(0)} + \{K^{(2)}[\tilde{\phi}^{(1)}]\} + \cdots, \tag{205}$$

where

$$\{K^{(2)}[\tilde{\phi}^{(1)}]\} = K_{+1}^{(2)}[\tilde{\phi}_{+1}^{(1)}] + K_{-1}^{(2)}[\tilde{\phi}_{-1}^{(1)}] \tag{206}$$

and

$$K_{\pm 1}^{(2)}[\tilde{\phi}_{\pm 1}^{(1)}] = \langle \tilde{\phi}_{\pm 1}^{(1)} \mid H_0^{(0)} - E_0^{(0)} \pm \hbar\omega \mid \tilde{\phi}_{\pm 1}^{(1)} \rangle + \langle \tilde{\phi}_{\pm 1}^{(1)} \mid h^{(1)} \mid \phi_0^{(0)} \rangle + \langle \phi_0^{(0)} \mid h^{(1)} \mid \tilde{\phi}_{\pm 1}^{(1)} \rangle. \tag{207}$$

In Eqs. (205)–(207) the functional $\{\operatorname{Re} K[\tilde{\phi}]\}$ through second order is expressed in terms of only the first-order trial functions $\tilde{\phi}_{+1}^{(1)}(\mathbf{r})$ and $\tilde{\phi}_{-1}^{(1)}(\mathbf{r})$. In carrying out the variation of the functional $\{\operatorname{Re} K[\tilde{\phi}]\}$ we can insure that the orthogonality condition [Eq.

[79] Demonstration of the existance of a set of quasiperiodic solutions of Eqs. (1), (28), and (41) for an adiabatically switched harmonic perturbation is somewhat problematic in general. See, for example, the discussions of Young and Deal (1970a, b) and Adamov and Balmakov (1971), who establish an adiabatic theorem for oscillatory Hamiltonians, and Epstein (1972), who establishes a similar theorem for variational wave functions. Here, we simply note that the more general choice of initial condition in Eq. (3b), $\Psi(\mathbf{r}, t \to -\infty) = \phi_k^{(0)} \exp[(i\hbar)^{-1} E_k^{(0)} t] \equiv \Psi_k^{(0)}(\mathbf{r}, t)$, gives rise to a set of solutions of Eq. (1)

$$\Psi_k(\mathbf{r}, t) = \chi_k(\mathbf{r}, t) \exp\left[(i\hbar)^{-1}\left(E_k^{(0)} t + \int_{-\infty}^{t} \operatorname{Re} \Delta E_k(t')\, dt'\right)\right],$$

which we assume to be in one-to-one correspondence with the unperturbed eigenstates $\Psi_k^{(0)}(\mathbf{r}, t)$. The $\tilde{\Psi}_k(\mathbf{r}, t)$ are easily shown to be orthonormal as a consequence of the orthonormality of the unperturbed eigenstates from which they evolve when the perturbation is applied. In the case of an adiabatically switched harmonic perturbation, the $\Psi_k(\mathbf{r}, t)$ are quasiperiodic, with associated level shifts $\Delta E_k$ [Eq. (49)], and describe the steady-state response of the system to the harmonic perturbation. The associated $\chi_k(\mathbf{r}, t)$ satisfying Eqs. (41) [$\operatorname{Re} \Delta E(t) \to \operatorname{Re} \Delta E_k(t)$] are periodic functions and are perfectly appropriate for the expansion of Eq. (198a), with the $\tilde{a}_k$ time independent.

[80] In the subsequent development we shall employ a perturbative approach to determine the level shift of Eq. (200). It will emerge there that when a trial function to first order in the perturbation is employed, the range of validity of Eq. (200) is limited to the normal dispersion frequency region, wherein the photon energy $\hbar\omega$ is insufficient to satisfy the Bohr condition for a transition to the resonance state. In second order, the range of validity of Eq. (200) is found to be limited to one-half the normal dispersion interval, and is further reduced in each order of perturbation theory. Consequently, in the case of an intense perturbation, for which high-order perturbation theory is required, we can anticipate that Eq. (200) will be limited to a low-frequency interval.

[81] At first sight it would appear inconsistent to employ Eq. (203) and yet retain terms in the functional to second order. However, if we employ the trial function $\tilde{\phi}(\mathbf{r}, t) = \phi_0^{(0)}(\mathbf{r}) + \tilde{\phi}^{(1)}(\mathbf{r}, t) + \tilde{\phi}^{(2)}(\mathbf{r}, t) + \cdots$ in the functional and retain terms to second order, we find that the second-order trial function $\tilde{\phi}^{(2)}(\mathbf{r}, t)$ does not contribute, provided that $\phi_0^{(0)}(\mathbf{r})$ is the correct unperturbed eigenfunction.

(182)] is satisfied to first order by requiring that

$$\langle \tilde{\phi}_{\pm 1}^{(1)} \mid \phi_0^{(0)} \rangle = 0. \tag{208}$$

Following the standard procedure, we employ Lagrangian multipliers $\lambda_{\pm 1}^{(1)}$ and introduce the functionals

$$L_{\pm 1}^{(2)}[\tilde{\phi}_{\pm 1}^{(1)}] = K_{\pm 1}^{(2)}[\tilde{\phi}_{\pm 1}^{(1)}] + (\lambda_{\pm 1}^{(1)})^* \langle \phi_0^{(0)} \mid \tilde{\phi}_{\pm 1}^{(1)} \rangle + \lambda_{\pm 1}^{(1)} \langle \tilde{\phi}_{\pm 1}^{(1)} \mid \phi_0^{(0)} \rangle. \tag{209}$$

The variational conditions

$$\delta L_{\pm 1}^{(2)}[\tilde{\phi}_{\pm 1}^{(1)}] = 0 \tag{210}$$

then give the equations

$$[H^{(0)}(\mathbf{r}) - E_0^{(0)} \pm \hbar\omega]\tilde{\phi}_{\pm 1}^{(1)}(\mathbf{r}) + [h^{(1)}(\mathbf{r}) + \lambda_{\pm 1}^{(1)}]\phi_0^{(0)}(\mathbf{r}) = 0 \tag{211}$$

for the functions $\tilde{\phi}_{\pm 1}^{(1)}(\mathbf{r})$. From Eqs. (211) and the requirement that $\tilde{\phi}_{\pm 1}^{(1)}(\mathbf{r})$ be orthogonal to $\phi_0^{(0)}(\mathbf{r})$ at the solution point [Eq. (208)], the Lagrangian multipliers are found to be

$$\lambda_{\pm 1}^{(1)} = -\langle \phi_0^{(0)} \mid h^{(1)} \mid \phi_0^{(0)} \rangle \equiv -\epsilon^{(1)}. \tag{212}$$

Consequently, we recognize Eqs. (211) as identical with the equations for $\phi_{\pm 1}^{(1)}(\mathbf{r})$ [Eq. (88a)] obtained in Sec. III directly from the Schrödinger equation.[82]

The variation conditions [Eq. (210)] insure that the functional $\{\mathrm{Re}\, K[\tilde{\phi}]\}$ is stationary to second order and guarantee that the orthogonality condition of Eq. (208) is satisfied at the solution point. The functionals [Eq. (209)] are identical with those previously obtained in the literature by simply constructing functionals whose stationary condition results in Eqs. (211). Here we have shown that Eqs. (209) arise from the perturbation expansion of the unified variational principle for the system level shift [Eqs. (190)], which, as we have demonstrated above, is a particular form of the Frenkel variational principle.

The level shift functional at the solution point $\tilde{\phi}^{(1)}(\mathbf{r}, t) = \phi^{(1)}(\mathbf{r}, t)$ becomes

$$\{\mathrm{Re}\, K[\phi]\} = E_0^{(0)} + \{K^{(2)}[\phi^{(1)}]\} + \cdots = E_0^{(0)} + K_{+1}^{(2)}[\phi_{+1}^{(1)}] + K_{-1}^{(2)}[\phi_{-1}^{(1)}] + \cdots \tag{213}$$

from Eq. (206). Employing Eqs. (207) and (211), this can be written as

$$\{\mathrm{Re}\, K[\phi]\} = E_0^{(0)} + \langle \phi_0^{(0)} \mid h^{(1)} \mid \phi_{+1}^{(1)} \rangle + \langle \phi_{-1}^{(1)} \mid h^{(1)} \mid \phi_0^{(0)} \rangle + \cdots \equiv E_0^{(0)} + \epsilon_0^{(2)} + \cdots \tag{214}$$

and, consequently, the level shift is determined to second order. Moreover, the variation-perturbation expression in Eq. (214) is in agreement with the level shift appearing in the wave function of Eq. (92), obtained directly from perturbative solution of the Schrödinger equation. The second variations of the functionals $K_{\pm 1}^{(2)}[\tilde{\phi}_{\pm 1}^{(1)}]$ are found to be positive at the solution points for $\omega < \omega_{10}$, where $\omega_{10}$ is the resonance frequency. Consequently, we obtain the bounding relation

$$\{K^{(2)}[\tilde{\phi}^{(1)}]\} \geq \{K^{(2)}[\phi^{(1)}]\} = \epsilon_0^{(2)} \qquad \omega < \omega_{10}, \tag{215}$$

and the range of validity of Eq. (200), when the level shift is determined to second-order by perturbation theory [Eq. (214)], is evidently limited to the normal dispersion frequency interval.[83]

To investigate the physical significance of the second-order term in the level shift of Eq. (214), we note from the time-dependent Hellmann–Feynman theorem [Eq. (51)] that $(t \to +\infty)$

$$\epsilon_0^{(2)} = \{K^{(2)}[\phi^{(1)}]\} = \tfrac{1}{2}\{\langle \Psi^{(0)} \mid V \mid \Psi^{(1)} \rangle + \langle \Psi^{(1)} \mid V \mid \Psi^{(0)} \rangle\}, \tag{216}$$

where

$$V(\mathbf{r}, t) = h(\mathbf{r})[\exp(i\omega t) + \exp(-i\omega t)]. \tag{217}$$

In the special case of the uniform-electric-field perturbation [Eqs. (102)], we find, employing Eqs. (91b), (104), and (105b), that Eq. (216), modified to include the perturbation parameter $\lambda$ [Eq. (102a)], becomes

$$\tfrac{1}{2}\epsilon_0^{(2)}(E^{(\omega)})^2 = (1/\tau)\int_t^{t+\tau} \boldsymbol{\mu}_\omega^{(1)}(t') \cdot \mathbf{E}^{(\omega)} \cos \omega t'\, dt', \tag{218}$$

where

$$\boldsymbol{\mu}_\omega^{(1)}(t) = E^{(\omega)} \mathbf{P}_\omega^{(1)} \cos \omega t \tag{219}$$

is the first-order contribution to the induced dipole moment [Eq. (104)] in phase with the electric field. The second-order level shift [Eq. (218)] in the case of an oscillating uniform electric field is found, therefore, to be simply the energy associated with the work done by the electric field on the polarization vector during the course of its induction (a.c. Stark shift).[42] In the static limit $\omega \to 0$, Eq. (219) becomes the induced static moment and Eq. (218) is the familiar Stark shift $\frac{1}{2}\alpha E^2$,

[82] In obtaining Eqs. (211) we have employed the variational principle of Eqs. (190), which requires the orthonormality condition of Eq. (182). If instead we were to employ the variational principle of Eq. (197), without the specific choice of Eq. (191) for $\tilde{\chi}(\mathbf{r}, t)$, the norm $\langle \tilde{\chi} \mid \tilde{\chi} \rangle$ would, in general, not be constant in time unless measures were taken to insure its constancy, such as the introduction of a Lagrangian multiplier. If the required measures are not taken, the development resulting from the use of Eq. (197) is invalid. This is the case in the computations of Chung (1968), who employs Eq. (197) without taking into account the necessary normalization demand. That his numerical results are nevertheless accurate is a consequence of the fact that the first-order trial function $\tilde{\chi}^{(1)}(\mathbf{r}, t)$ he employs is orthogonal to $\chi^{(0)}(\mathbf{r})$ and so the norm deviates from unity only in second-order. Presumably, the convergence difficulties Chung experienced in the neighborhood of the helium resonance frequency might be avoided by proper treatment of the normalization condition, since near resonance the first-order functions will grow large and $\langle \tilde{\chi} \mid \tilde{\chi} \rangle = \langle \tilde{\chi}^{(1)} \mid \tilde{\chi}^{(1)} \rangle$ will eventually diverge as $\omega \to \omega_{10}$.

[83] The functional $K_{+1}^{(2)}[\tilde{\phi}_{+1}^{(1)}]$ has a positive second variation at the solution point for all applied frequencies. It is the $K_{-1}^{(2)}[\tilde{\phi}_{-1}^{(1)}]$ functional that limits the range of validity of Eq. (215) to the normal dispersion region. A variety of procedures can be employed to extend the frequency interval over which Eq. (215) applies and to construct complementary lower bounds. See, for example, Adamov, Orlov, and Rebane (1968), Kolker (1968), and Robinson (1969a, b).

where $\alpha$ is the static dipole polarizability and $E$ is the static electric field strength.[84]

Assuming that $\phi^{(1)}(\mathbf{r},t)$ has been determined exactly, we can proceed to the evaluation of the second-order function $\phi^{(2)}(\mathbf{r},t)$. Employing the ansatz

$$\tilde{\phi}(\mathbf{r},t)=\phi^{(0)}(\mathbf{r})+\phi^{(1)}(\mathbf{r},t)+\tilde{\phi}^{(2)}(\mathbf{r},t)+\cdots \quad (220)$$

in Eqs. (190) gives, retaining terms through fourth order,[85]

$$\{\mathrm{Re}\,K[\tilde{\phi}]\}=E_0^{(0)}+\epsilon_0^{(2)}+\{K^{(4)}[\tilde{\phi}^{(2)}] -E^{(2)}(t)\langle\phi^{(1)}\mid\phi^{(1)}\rangle\}+\cdots, \quad (221)$$

where

$$\{K^{(4)}[\tilde{\phi}^{(2)}]\}=\{\langle\tilde{\phi}^{(2)}\mid H^{(0)}-E_0^{(0)}-i\hbar(\partial/\partial t)\mid\tilde{\phi}^{(2)}\rangle +\langle\tilde{\phi}^{(2)}\mid H^{(1)}-E^{(1)}\mid\phi^{(1)}\rangle+\langle\phi^{(1)}\mid H^{(1)}-E^{(1)}\mid\tilde{\phi}^{(2)}\rangle\}. \quad (222)$$

From Eq. (87b) we see that the appropriate form for the trial function $\tilde{\phi}^{(2)}(\mathbf{r},t)$ is

$$\tilde{\phi}^{(2)}(\mathbf{r},t)=\tilde{\phi}_{+2}^{(2)}(\mathbf{r})\exp(i2\omega t) +\tilde{\phi}_{-2}^{(2)}(\mathbf{r})\exp(-i2\omega t)+\tilde{\phi}_0^{(2)}(\mathbf{r}). \quad (223)$$

Employing Eq. (223) in Eq. (222) gives

$$\{K^{(4)}[\tilde{\phi}^{(2)}]\}=K_{+2}^{(4)}[\tilde{\phi}_{+2}^{(2)}]+K_{-2}^{(4)}[\tilde{\phi}_{-2}^{(2)}] +K_0^{(4)}[\tilde{\phi}_0^{(2)}], \quad (224)$$

where

$$K_{\pm2}^{(4)}[\tilde{\phi}_{\pm2}^{(2)}]=\langle\tilde{\phi}_{\pm2}^{(2)}\mid H^{(0)}-E_0^{(0)}\pm2\hbar\omega\mid\tilde{\phi}_{\pm2}^{(2)}\rangle +\langle\tilde{\phi}_{\pm2}^{(2)}\mid h^{(1)}-\epsilon^{(1)}\mid\phi_{\pm1}^{(1)}\rangle+\langle\phi_{\pm1}^{(1)}\mid h^{(1)}-\epsilon^{(1)}\mid\tilde{\phi}_{\pm2}^{(2)}\rangle, \quad (225a)$$

and

$$K_0^{(4)}[\tilde{\phi}_0^{(2)}]=\langle\tilde{\phi}_0^{(2)}\mid H^{(0)}-E_0^{(0)}\mid\tilde{\phi}_0^{(2)}\rangle +\langle\tilde{\phi}_0^{(2)}\mid h^{(1)}-\epsilon^{(1)}\mid\phi_{+1}^{(1)}+\phi_{-1}^{(1)}\rangle +\langle\phi_{+1}^{(1)}+\phi_{-1}^{(1)}\mid h^{(1)}-\epsilon^{(1)}\mid\tilde{\phi}_0^{(2)}\rangle. \quad (225b)$$

The functional $\{\mathrm{Re}\,K[\tilde{\phi}]\}$, through fourth order, depends only on the trial functions $\tilde{\phi}_{\pm2}^{(2)}(\mathbf{r})$ and $\tilde{\phi}_0^{(2)}(\mathbf{r})$, which are subject to the second-order orthogonality constraints [Eq. (182)]

$$\langle\tilde{\phi}_{\pm2}^{(2)}\mid\phi_0^{(0)}\rangle=0, \quad (226a)$$

$$\langle\tilde{\phi}_0^{(2)}\mid\phi_0^{(0)}\rangle=0. \quad (226b)$$

Following the standard procedure, we introduce Lagrangian multipliers $\lambda_{\pm2}^{(2)}$ and $\lambda_0^{(2)}$ and the functionals

$$L_{\pm2}^{(4)}[\tilde{\phi}_{\pm2}^{(2)}]=K_{\pm2}^{(4)}[\tilde{\phi}_{\pm2}^{(2)}]+(\lambda_{\pm2}^{(2)})^*\langle\phi_0^{(0)}\mid\tilde{\phi}_{\pm2}^{(2)}\rangle +\lambda_{\pm2}^{(2)}\langle\tilde{\phi}_{\pm2}^{(2)}\mid\phi_0^{(0)}\rangle, \quad (227a)$$

$$L_0^{(4)}[\tilde{\phi}_0^{(2)}]=K_0^{(4)}[\tilde{\phi}_0^{(2)}]+(\lambda_0^{(2)})^*\langle\phi_0^{(0)}\mid\tilde{\phi}_0^{(2)}\rangle +\lambda_0^{(2)}\langle\tilde{\phi}_0^{(2)}\mid\phi_0^{(0)}\rangle. \quad (227b)$$

The variation conditions

$$\delta L_{\pm2}^{(4)}[\tilde{\phi}_{\pm2}^{(2)}]=0, \qquad \delta L_0^{(4)}[\tilde{\phi}_0^{(2)}]=0 \quad (228)$$

then give the equations

$$[H^{(0)}(\mathbf{r})-E_0^{(0)}\pm2\hbar\omega]\tilde{\phi}_{\pm2}^{(2)}(\mathbf{r})+[h^{(1)}(\mathbf{r})-\epsilon^{(1)}]\phi_{\pm1}^{(1)}(\mathbf{r}) +\lambda_{\pm2}^{(2)}\phi_0^{(0)}(\mathbf{r})=0, \quad (229a)$$

$$[H^{(0)}(\mathbf{r})-E_0^{(0)}]\tilde{\phi}_0^{(2)}(\mathbf{r}) +[h^{(1)}(\mathbf{r})-\epsilon^{(1)}][\phi_{+1}^{(1)}(\mathbf{r})+\phi_{-1}^{(1)}(\mathbf{r})] +\lambda_0^{(2)}\phi_0^{(0)}(\mathbf{r})=0. \quad (229b)$$

From the requirements that $\tilde{\phi}_{\pm2}^{(2)}(\mathbf{r})$ and $\tilde{\phi}_0^{(2)}(\mathbf{r})$ be orthogonal to $\phi_0^{(0)}(\mathbf{r})$ at the solution point, the Lagrangian multipliers are

$$\lambda_{\pm2}^{(2)}=-\langle\phi_0^{(0)}\mid h^{(1)}\mid\phi_{\pm1}^{(1)}\rangle\equiv-\epsilon_{\pm2}^{(2)}, \quad (230a)$$

$$\lambda_0^{(2)}=-\epsilon_{+2}^{(2)}-\epsilon_{-2}^{(2)}=-\epsilon_0^{(2)}. \quad (230b)$$

Thus, Eqs. (229) are identical with the equations for $\phi_{\pm2}^{(2)}(\mathbf{r})$ and $\phi_0^{(2)}(\mathbf{r})$ [Eqs. (88b) and (88c)] obtained in Sec. III directly from the Schrödinger equation.

The level-shift functional at the solution point $\tilde{\phi}^{(2)}(\mathbf{r},t)=\phi^{(2)}(\mathbf{r},t)$ takes the form

$$\{\mathrm{Re}\,K[\phi]\}=E_0^{(0)}+\epsilon_0^{(2)} +\{K^{(4)}[\phi^{(2)}]-E^{(2)}\langle\phi^{(1)}\mid\phi^{(1)}\rangle\}+\cdots \equiv E_0^{(0)}+\epsilon_0^{(2)}+\epsilon_0^{(4)}+\cdots, \quad (231)$$

where $\{K^{(4)}[\phi^{(2)}]\}$ is given by Eq. (224) with

$$K_{\pm2}^{(4)}[\phi_{\pm2}^{(2)}]=\langle\phi_{\pm1}^{(1)}\mid h^{(1)}-\epsilon^{(1)}\mid\phi_{\pm2}^{(2)}\rangle, \quad (232a)$$

$$K_0^{(4)}[\phi_0^{(2)}]=\langle\phi_{+1}^{(1)}+\phi_{-1}^{(1)}\mid h^{(1)}-\epsilon^{(1)}\mid\phi_0^{(2)}\rangle, \quad (232b)$$

and where

$$\{E^{(2)}\langle\phi^{(1)}\mid\phi^{(1)}\rangle\}=(\langle\phi_{+1}^{(1)}\mid\phi_{+1}^{(1)}\rangle+\langle\phi_{-1}^{(1)}\mid\phi_{-1}^{(1)}\rangle)\epsilon_0^{(2)} +\langle\phi_{+1}^{(1)}\mid\phi_{-1}^{(1)}\rangle\epsilon_{+2}^{(2)}+\langle\phi_{-1}^{(1)}\mid\phi_{+1}^{(1)}\rangle\epsilon_{-2}^{(2)}. \quad (232c)$$

Equations (232a) and (232b) are obtained from Eqs. (225) by making use of the fact that Eqs. (229) are satisfied at the solution point, and Eq. (232c) is obtained using Eqs. (87a) and (89b). The second variations of the functionals $K_{\pm2}^{(4)}[\tilde{\phi}_{\pm2}^{(2)}]$ and $K_0^{(4)}[\tilde{\phi}_0^{(2)}]$ are found to be positive at the solution points for $2\omega<\omega_{10}$, where $\omega_{10}$ is the resonance frequency. Consequently, we obtain the bounding relation

$$\{K^{(4)}[\tilde{\phi}^{(2)}]-E^{(2)}(t)\langle\phi^{(1)}\mid\phi^{(1)}\rangle\}\geq\{K^{(4)}[\phi^{(2)}] -E^{(2)}(t)\langle\phi^{(1)}\mid\phi^{(1)}\rangle\}=\epsilon_0^{(4)}, \qquad 2\omega<\omega_{10}, \quad (233)$$

[84] A variety of recent computational applications have employed the procedures of Eqs. (203)–(219) for determinations of the dynamic and static polarizabilities, $\mathbf{P}_\omega^{(1)}$, and related level shifts, $\epsilon_0^{(2)}$, of simple atoms and molecules. See, for example, Karplus (1964), Chan and Dalgarno (1965), Kolker and Michels (1965), Kolos and Wolniewicz (1967), Victor, Browne, and Dalgarno (1967), Chung (1968), and Kamikawai, Watanabe, and Amemiya (1969).

[85] As remarked in Footnote 81, it might appear at first somewhat inconsistent to employ Eq. (220) and yet retain terms to fourth order in the functional. However, if we enter the functional of Eqs. (190) with the trial function $\tilde{\phi}(\mathbf{r},t)=\phi_0^{(0)}(\mathbf{r})+\phi^{(1)}(\mathbf{r},t)+\tilde{\phi}^{(2)}(\mathbf{r},t)+\tilde{\phi}^{(3)}(\mathbf{r},t)+\tilde{\phi}^{(4)}(\mathbf{r},t)+\cdots$, and retain terms to fourth order, Eq. (221) is nevertheless obtained, provided that $\phi_0^{(0)}(\mathbf{r})$ and $\phi^{(1)}(\mathbf{r},t)$ are the correct solutions of the static eigenvalue problem and of Eqs. (204) and (211), respectively.

and the range of validity of Eq. (200) is now limited to one-half the normal dispersion interval.[86] Equation (231) evidently provides a perturbation approximation to the level shift through fourth order, even though the wave function is known only to second order. This result is a special case of the general "$2n+1$" theorem for time-dependent perturbation theory.[87]

To investigate the physical significance of the fourth-order level shift $\epsilon_0^{(4)}$, we note from the time dependent Hellmann–Feynman theorem [Eq. (51)] that $(t\rightarrow+\infty)$,

$$\epsilon_0^{(4)}=\tfrac{1}{4}\{\langle\Psi^{(0)}\mid V\mid\Psi^{(3)}\rangle+\langle\Psi^{(3)}\mid V\mid\Psi^{(0)}\rangle+\langle\Psi^{(1)}\mid V\mid\Psi^{(2)}\rangle+\langle\Psi^{(2)}\mid V\mid\Psi^{(1)}\rangle\}, \quad (234)$$

where $V(\mathbf{r},t)$ is given by Eq. (217). In the special case of a uniform-electric-field perturbation [Eqs. (102)], we find

$$\tfrac{1}{4}\epsilon_0^4(E^{(\omega)})^4=(1/\tau)\int_t^{t+\tau}\boldsymbol{\mu}_\omega^{(3)}(t')\cdot\mathbf{E}^{(\omega)}\cos\omega t'\,dt', \quad (235)$$

where

$$\boldsymbol{\mu}_\omega^{(3)}(t)=(E^{(\omega)})^3\mathbf{P}_\omega^{(3)}\cos\omega t \quad (236)$$

is the third-order contribution to the induced moment [Eq. (104)] that is in phase with the electric field. Consequently, the fourth-order ac Stark shift in a uniform electric field is similar in form to the second-order shift of Eq. (218).[88] Similarly, in higher-order the level shifts also correspond to the time average of the scalar product of the applied electric field with the component of induced moment that is in phase with the field. Thus, the complete level shift in this case is simply the energy acquired by the system due to the work done by the external electric field on the electric dipole moment during the course of its induction.

[86] As in the case of Eq. (215), the restriction of Eq. (233) to half the normal dispersion region, $2\omega<\omega_{10}$, is due to the $K_{-2}^{(4)}[\tilde{\phi}_{-2}^{(2)}]$ functional, which has a positive second variation only in this interval.

[87] If the wave function is known to order $n$ in some perturbation parameter $\lambda[\phi(\mathbf{r},t)=\tilde{\phi}(\mathbf{r},t)+O(\lambda^n)]$, then it is clear that since the functionals of Eqs. (190) and (197) are stationary to second order in the error in the wave function they are known to order $2n+1[\{\text{Re } K[\phi]\}=\{\text{Re } K[\tilde{\phi}]\}+O(\lambda^{2n+1})]$; that is, the variational principle of Eqs. (190) and (197) insures the existence of a "$2n+1$" theorem for the variational functionals, similar to that for the energy in the static case. Consequently, from the time-dependent Hellmann–Feynman theorem [Eq. (51)], we see that the response of the system $\{\langle\Psi\mid H^{(1)}\mid\Psi\rangle\}$ is known to $O(\lambda^{2n})$ if the wave function is known to order $n$. Further discussion of the $2n+1$ theorem for time-dependent perturbation theory is given by Epstein (1969). For related discussion of the static case see Epstein (1968b). Although correct in its essentials, this latter paper perhaps does not make it sufficiently clear that the $2n+1$ theorem applies to *any* variational calculation whatsoever. For clarification of this point see Epstein (1971). The $2n+1$ theorems in the static and time-dependent cases also imply the existence of "interchange" theorems for variational calculations. For discussion of these corollary theorems in the case of exact wavefunctions, see, for example, Hirschfelder, Byers-Brown, and Epstein (1964), Sec. IX.B.

[88] Variational calculations of nonlinear optical susceptibilities, $\mathbf{P}_\omega^{(3)}$ and $\mathbf{P}_{3\omega}^{(3)}$, and the associated level shift of Eq. (235), which employ the development of Eqs. (220)–(236), are given, for example, by Sitz and Yaris (1968) and Grasso, Chung, and Hurst (1968).

### C. Hartree–Fock Approximations

The development of the preceding section for an harmonic perturbation can be employed in the Hartree–Fock approximation to obtain variational equations suitable for computational applications.

*Uncoupled Hartree–Fock Theory*

A variational formulation of the first-order uncoupled Hartree–Fock approximation described in Sec. III is obtained from the development of Eqs. (203)–(219) by introducing the trial functions

$$\tilde{\phi}_{\pm1}^{(1)}(\mathbf{r})=\sum_{i=1}^{N}\tilde{U}_{i\pm}^{(1)}(\mathbf{r}), \quad (237)$$

where, in the notation of Eq. (117),

$$\tilde{U}_{i\pm}^{(1)}(\mathbf{r})=(N!)^{-1/2}\det\mid u_1^{(0)}(\mathbf{r}_1)u_2^{(0)}(\mathbf{r}_2)\cdots\times u_{i-1}^{(0)}(\mathbf{r}_{i-1})\tilde{u}_{i\pm}^{(1)}(\mathbf{r}_i)u_{i+1}^{(0)}(\mathbf{r}_{i+1})\cdots u_N^{(0)}(\mathbf{r}_N)\mid. \quad (238)$$

We employ the unperturbed Hartree–Fock Hamiltonian and energy [Eqs. (108)] in place of the correct zeroth-order Hamiltonian and energy, respectively, and in accordance with the remarks following Eqs. (121), we will require without loss of generality that

$$\langle u_i^{(0)}\mid\tilde{u}_{i\pm}^{(1)}\rangle=0 \qquad i=1,2,\cdots,N, \quad (239a)$$

and

$$\langle\tilde{u}_{j\pm}^{(1)}\mid u_i^{(0)}\rangle+\langle u_j^{(0)}\mid\tilde{u}_{i\mp}^{(1)}\rangle=0 \qquad i,j=1,2,\cdots,N. \quad (239b)$$

Equation (239a) clearly insures that the orthogonality requirement [Eq. (118)] is satisfied. Introducing Eqs. (237) and (238) and the Hartree–Fock Hamiltonian and energy into the $K_{\pm1}^{(2)}[\tilde{\phi}_{\pm1}^{(1)}]$ functionals [Eq. (207)] for the perturbation of Eq. (80), and incorporating the orthogonality requirements of Eqs. (239) by means of Lagrangian multipliers $\lambda_{ij}^{(1)}(\pm)$, gives

$$L_{\pm1}^{(2)}[\tilde{\phi}_{\pm1}^{(1)}]=\sum_{i=1}^{N}L_{i\pm}^{(2)}[\tilde{u}_{i\pm}^{(1)}], \quad (240)$$

where

$$\begin{aligned}L_{i\pm}^{(2)}[\tilde{u}_{i\pm}^{(1)}]=&\langle\tilde{u}_{i\pm}^{(1)}\mid h^{(0)}-\epsilon_i^{(0)}\pm\hbar\omega\mid\tilde{u}_{i\pm}^{(1)}\rangle\\&+\langle\tilde{u}_{i\pm}^{(1)}\mid h^{(1)}+\lambda_{ii}^{(1)}(\pm)\mid u_i^{(0)}\rangle\\&+\langle u_i^{(0)}\mid h^{(1)}+\lambda_{ii}^{(1)}(\pm)^*\mid\tilde{u}_{i\pm}^{(1)}\rangle\\&+\sum_{j=1}^{N}(j\neq i)[\langle\tilde{u}_{i\pm}^{(1)}\mid u_j^{(0)}\rangle\lambda_{ij}^{(1)}(\pm)\\&+\lambda_{ij}^{(1)}(\pm)^*\langle u_j^{(0)}\mid\tilde{u}_{i\pm}^{(1)}\rangle\mp\hbar\omega\mid\langle\tilde{u}_{i\pm}^{(1)}\mid u_j^{(0)}\rangle\mid^2].\end{aligned} \quad (241)$$

Here, $h^{(0)}(\mathbf{r}_i)$ is the unperturbed Fock operator [Eqs. (109)] and $h^{(1)}(\mathbf{r}_i)$ is the spatial part of the one-particle harmonic perturbation [Eq. (114)]. The variational conditions [Eq. (210)]

$$\delta L_{\pm1}^{(2)}[\tilde{\phi}_{\pm1}^{(1)}]=0 \quad (242)$$

are satisfied by the individual requirements

$$\delta L_{i\pm}^{(2)}[\tilde{u}_{i\pm}^{(1)}]=0 \qquad i=1, 2, \cdots, N, \tag{243}$$

which give the equations,

$$[h^{(0)}(\mathbf{r}_i)-\epsilon_i^{(0)}\pm\hbar\omega]\tilde{u}_{i\pm}^{(1)}(\mathbf{r}_i) + [h^{(1)}(\mathbf{r}_i)-\epsilon_i^{(1)}]u_i^{(0)}(\mathbf{r}_i)=0, \tag{244}$$

where we have introduced the choice of multipliers

$$\lambda_{ii}^{(1)}(\pm)=-\langle u_i^{(0)} \mid h^{(1)} \mid u_i^{(0)}\rangle\equiv-\epsilon_i^{(1)}, \tag{245a}$$

$$\lambda_{ij}^{(1)}(\pm)=\pm\hbar\omega\langle u_j^{(0)} \mid u_{i\pm}^{(1)}\rangle. \tag{245b}$$

We see that the orthogonality requirements of Eqs. (239) are an immediate consequence of Eq. (244).

It is clear that Eq. (244) is in agreement with the equation obtained from Eq. (120) in the case of an harmonic potential, employing the time-dependent spin–orbital

$$u_i^{(1)}(\mathbf{r}_i, t)=u_{i+}^{(1)}(\mathbf{r}_i)\exp(i\omega t)+u_{i-}^{(1)}(\mathbf{r}_i)\exp(-i\omega t). \tag{246}$$

Consequently, the variational conditions of Eq. (243) are equivalent to the uncoupled Hartree–Fock equations [Eq. (120)] for an harmonic perturbation, and insure that the resulting orbitals satisfy the orthogonality condition of Eqs. (239) at the solution point.[89] Moreover, from Eqs. (214) and (237) we have

$$\epsilon_{\mathrm{HF}}^{(2)}=\{K_{\mathrm{HF}}^{(2)}[\phi_{\mathrm{HF}}^{(1)}]\}=\sum_{i=1}^{N}(\langle u_i^{(0)} \mid h^{(1)} \mid u_{i+}^{(1)}\rangle + \langle u_{i-}^{(1)} \mid h^{(1)} \mid u_i^{(0)}\rangle) \tag{247}$$

and from the second variation of the functionals of Eq. (241) at the solution point we obtain

$$\{K_{\mathrm{HF}}^{(2)}[\tilde{\phi}_{\mathrm{HF}}^{(1)}]\}\geq\{K_{\mathrm{HF}}^{(2)}[\phi_{\mathrm{HF}}^{(1)}]\}=\epsilon_{\mathrm{HF}}^{(2)} \qquad \omega<\omega_{10}, \tag{248}$$

where $\omega_{10}$ is the resonance frequency of the Fock operator. Thus, the functionals of Eq. (241) provide computationally convenient expressions that lead to a bound on the uncoupled Hartree–Fock approximation to the second-order level shift.[90]

### *Coupled Hartree–Fock Theory*

The uncoupled functionals of Eq. (241) are computationally convenient and avoid the necessity of finding a self-consistent solution in first-order. More accurate results are provided by the coupled Hartree–Fock approximation,[91] which entails a first-order self-consistency requirement, as in the familiar Hartree–Fock approximation to the unperturbed wave function.

The coupled Hartree–Fock equations are conveniently derived from the Frenkel principle [Eq. (178)] employing a trial function in the form of the Slater determinant

$$\tilde{\Psi}_{\mathrm{HF}}(r, t)=(N!)^{-1/2}\mid\tilde{u}_1(\mathbf{r}_1, t)\tilde{u}_2(\mathbf{r}_2, t)\cdots\tilde{u}_N(\mathbf{r}_N, t)\mid, \tag{249}$$

containing $N$ trial spin–orbitals $\tilde{u}_i(\mathbf{r}_i, t)$ which satisfy the customary orthonormality requirement

$$\langle\tilde{u}_i \mid \tilde{u}_j\rangle=\delta_{ij} \qquad i, j=1, 2, \cdots, N. \tag{250}$$

Substituting Eq. (249) into Eq. (178), written for an $N$-electron atom in the Coulomb approximation, with the perturbation Hamiltonian given by Eq. (114), we find

$$\delta\langle\tilde{\Psi}_{\mathrm{HF}} \mid H^{(0)}+H^{(1)}-i\hbar(\partial/\partial t) \mid \tilde{\Psi}_{\mathrm{HF}}\rangle + i\hbar(\partial/\partial t)\langle\Psi_{\mathrm{HF}} \mid \partial\tilde{\Psi}_{\mathrm{HF}}\rangle = \sum_{i=1}^{N}(\langle\delta\tilde{u}_i \mid h+g^{(1)}-i\hbar(\partial/\partial t) \mid \tilde{u}_i\rangle + \text{complex conjugate}). \tag{251}$$

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[89] The functionals of Eqs. (241)–(245) do not agree with those obtained previously by Karplus and Kolker (1963b) and Heinrichs (1968c) since they do not employ our choice of multipliers [Eqs. (245)]. However, if this choice is introduced into their developments, which does not limit the generality of the procedure, the results of Karplus and Kolker and of Heinrichs are identical with Eqs. (241)–(242). Alternatively, if the orthogonality requirements of Eqs. (239) are satisfied in our development by Schmidt orthogonalizing the trial spin–orbitals $\tilde{u}_{i+1}^{(1)}(\mathbf{r}_i)$ to all the unperturbed orbitals, the functional of Eq. (241) becomes identical with that of Karplus and Kolker. Related discussion of this point in the static case is given by Langhoff and Hurst (1965). Consequently, our development is essentially identical with those of Karplus and Kolker and of Heinrichs, as discussed in Footnote 68. The functionals of Chung (1967) however, disagree with our results in an essential way. Chung obtains spurious coupling terms between first-order orbitals in his Eq. (53) due to the failure to identify the secular terms in his functional of Eq. (52). In particular, the third term from the last on the right-hand side of Eq. (53) can only arise from a secular term in the first-order wave function and its inclusion is inconsistent with his preceding development, which is designed to extract such terms.

[90] The Fock operator [Eqs. (109)] for a neutral atom or molecule generally has no bound excited states. See, for example, Kelly (1963) and Epstein (1964) for discussion of this point. Consequently, we might suspect that the uncoupled Hartree–Fock approximation will give a poor approximation in certain instances to the excitation spectra, or related physical properties, of atoms or molecules. This is illustrated by the beryllium atom computations of Levine and Taylor (1964), who obtain a dynamic polarizability that exhibits a continuous behavior in the frequency region of experimental resonances. This unsatisfactory aspect of the uncoupled Hartree–Fock approximation has led to the introduction of a variety of alternative uncoupled approximations to both static and time-dependent perturbation theory, similar to the original approximation of Karplus and Kolker (1963b) discussed in Footnote 68. For intercomparisons of these approximations in the closely related static case, see, for example, Langhoff, Karplus, and Hurst (1966), Caves and Karplus (1969), and Sadlej and Jaszunski (1971), and references cited therein.

[91] The time-dependent Hartree–Fock theory was first discussed by Dirac (1930), and subsequently in perturbative form by Dalgarno and Victor (1966), and Heinrichs (1968c). The method is also designated as the random phase approximation with exchange. See, for example, Thouless (1961), McLachlan and Ball (1963), and Rowe (1968), and references cited therein.

In Eq. (251), $h(\mathbf{r}_i, t)$ is the Fock operator

$$h(\mathbf{r}_i, t) = -(\hbar^2/2m)\nabla_i^2 - (Ze^2/r_i) + v(\mathbf{r}_i, t), \quad (252a)$$

with the nonlocal Fock potential

$$v(\mathbf{r}_i, t) = \sum_{j=1}^{N} \langle \tilde{u}_j | (e^2/r_{ij})(1-P_{ij}) | \tilde{u}_j \rangle, \quad (252b)$$

and $g^{(1)}(\mathbf{r}_i, t)$ the one-electron perturbation operator [Eq. (114)]. We insure that the variations $\delta\tilde{u}_i(\mathbf{r}_i, t)$ in Eq. (251) are consistent with the orthonormality constraints by introducing Lagrangian multipliers, $\lambda_{ij}(t)$, chosen to satisfy Eqs. (250). Setting the right hand side of Eq. (251) equal to zero and incorporating the orthormality requirements, we obtain

$$[h(\mathbf{r}_i, t) + g^{(1)}(\mathbf{r}_i, t) - i\hbar(\partial/\partial t)]\tilde{u}_i(\mathbf{r}, t) + \sum_{j=1}^{N} \lambda_{ij}(t)\tilde{u}_j(\mathbf{r}_i, t) = 0. \quad (253)$$

These are the general time-dependent Hartree–Fock equations for the spin–orbitals $\tilde{u}_i(\mathbf{r}_i, t)$.

Various choices for the Lagrangian multipliers $\lambda_{ij}(t)$ which insure that Eqs. (250) are satisfied can be made. The particularly simple choice

$$\lambda_{ij}(t) \equiv 0 \qquad i, j, = 1, 2, \cdots, N, \quad (254)$$

results in the canonical time-dependent Hartree–Fock equations

$$[h(\mathbf{r}_i, t) + g^{(1)}(\mathbf{r}_i, t) - i\hbar(\partial/\partial t)]u_i(\mathbf{r}_i, t) = 0. \quad (255)$$

That the choice of Eq. (254) satisfies Eqs. (250) at the solution point follows from Eq. (255) and the Hermitian nature of the Fock operator and the perturbation Hamiltonian; we find, from Eq. (255) that

$$(\partial/\partial t)\langle u_j | u_i \rangle = 0 \quad (256)$$

and, consequently, Eqs. (250) are satisfied at all times if they are satisfied initially ($t \rightarrow -\infty$).

Equations (255) are similar in form to the complete time-dependent Schrödinger equation [Eq. (1)], aside from the self-consistency requirement implied by the form of the Hermitian operator of Eqs. (252). We can, therefore, apply the development of Sec. II.B to eliminate the normalization and secular terms that arise in the perturbation solution of Eq. (255). Following the development of Sec. II, we find that the solutions $u_i(\mathbf{r}_i, t)$ of Eq. (255) take the form

$$u_i(\mathbf{r}_i, t) = \phi_i(\mathbf{r}_i, t)\langle \phi_i | \phi_i \rangle^{-1/2} \times \exp\left((i\hbar)^{-1}\int_{-\infty}^{t} \mathrm{Re}\,\epsilon_i(t')\,dt'\right), \quad (257)$$

where

$$\epsilon_i(t) = \langle \phi_i^{(0)} | h + g^{(1)} | \phi_i \rangle \equiv \epsilon_i^{(0)} + \Delta\epsilon_i(t), \quad (258)$$

$$\langle \phi_i^{(0)} | \phi_i \rangle = 1, \quad (259)$$

and the regular part of the spin–orbital, $\phi_i(\mathbf{r}_i, t)$ satisfies

$$[h(\mathbf{r}_i, t) - \epsilon_i^{(0)} - i\hbar(\partial/\partial t)]\phi_i(\mathbf{r}_i, t) + [g^{(1)}(\mathbf{r}_i, t) - \Delta\epsilon_i(t)]\phi_i(\mathbf{r}_i, t) = 0. \quad (260)$$

Introducing the perturbation expansions

$$\phi_i(\mathbf{r}_i, t) = \sum_{n=0}^{\infty} \phi_i^{(n)}(\mathbf{r}_i, t), \quad (261a)$$

$$\Delta\epsilon_i(t) = \sum_{n=1}^{\infty} \epsilon_i^{(n)}(t), \quad (261b)$$

into Eq. (260) gives, through first order,

$$[h^{(0)}(\mathbf{r}_i) - \epsilon_i^{(0)}]\phi_i^{(0)}(\mathbf{r}_i) = 0 \quad (262a)$$

$$[h^{(0)}(\mathbf{r}_i) - \epsilon_i^{(0)} - i\hbar(\partial/\partial t)]\phi_i^{(1)}(\mathbf{r}_i, t) + [g^{(1)}(\mathbf{r}_i, t) + v^{(1)}(\mathbf{r}_i, t) - \epsilon_i^{(1)}(t)]\phi_i^{(0)}(\mathbf{r}_i) = 0 \quad (262b)$$

where

$$h^{(0)}(\mathbf{r}_i) = -(\hbar^2/2m)\nabla_i^2 - (Ze^2/r_i) + \sum_{j=1}^{N} \langle \phi_j^{(0)} | (e^2/r_{ij})(1-P_{ij}) | \phi_j^{(0)} \rangle \quad (263a)$$

$$v^{(1)}(\mathbf{r}_i, t) = \sum_{j=1}^{N} (\langle \phi_j^{(1)} | (e^2/r_{ij})(1-P_{ij}) | \phi_j^{(0)} \rangle + \langle \phi_j^{(0)} | (e^2/r_{ij})(1-P_{ij}) | \phi_j^{(1)} \rangle), \quad (263b)$$

and

$$\epsilon_i^{(1)}(t) = \langle \phi_i^{(0)} | v^{(1)} + g^{(1)} | \phi_i^{(0)} \rangle. \quad (264)$$

We recognize Eq. (262a) as the familiar unperturbed Hartree–Fock equation in canonical form, and Eq. (262b) is the first-order, time-dependent, coupled Hartree–Fock equation. Evidently there are coupling terms between first-order orbitals in Eq. (262b) due to the presence of $v^{(1)}(\mathbf{r}_i, t)$ [Eq. (263b)]. This introduces the necessity of a first-order self-consistent solution and results in the designation of this approximation as the "coupled" Hartree–Fock approximation. By contrast, the first-order equations in the uncoupled approximation [Eq. (244)] do not entail a self-consistent solution. The higher-order coupled Hartree–Fock equations are obtained by including additional terms in the expansion of Eq. (260).[92]

[92] The higher-order coupled Hartree–Fock equations are discussed and employed, for example, by Langhoff, Lyons, and Hurst (1966), Lyons, Langhoff, and Hurst (1966), Klingbeil, Kaveeshwar, and Hurst (1971), and Sitter and Hurst (1972).

It is of interest to note that the canonical choice of Lagrangian multipliers [Eq. (254)] employed to obtain Eq. (255) gives rise to an over-all phase factor in the Hartree–Fock wave function that is different from the phase factor we have identified in the exact wave function [Eq. (33)]. That is, from Eqs. (249) and (257), we have,

$$\Psi_{\mathrm{HF}}(\mathbf{r},t)=(N!)^{-1/2}\det|\,\chi_1(\mathbf{r}_1,t)\chi_2(\mathbf{r}_2,t)\cdots\chi_N(\mathbf{r}_N,t)\,|\times\exp\left[(i\hbar)^{-1}\sum_{i=1}^{N}\int_{-\infty}^{t}\mathrm{Re}\,\epsilon_i(t')\,dt'\right],\quad(265)$$

where

$$\chi_i(\mathbf{r}_i,t)=\phi_i(\mathbf{r}_i,t)\,\langle\phi_i\,|\,\phi_i\rangle^{-1/2}.\quad(266)$$

It is clear that the phase factor of Eq. (265) is distinct from that in the correct wave function [Eq. (33)]. In particular, for the unperturbed problem, Eq. (265) becomes

$$\Psi_{\mathrm{HF}}^{(0)}(\mathbf{r},t)=(N!)^{-1/2}\det|\,\phi_1^{(0)}(\mathbf{r}_1)\phi_2^{(0)}(\mathbf{r}_2)\cdots\phi_N^{(0)}(\mathbf{r}_N)\,|\times\exp\left[(i\hbar)^{-1}\sum_{i=1}^{N}\epsilon_i^{(0)}t\right],\quad(267)$$

and the resulting phase factor differs from the Hartree–Fock energy [Eq. (108b)] by including the Coulomb repulsion integrals twice.

Although it has no practical consequences as far as expectation values are concerned, it is perhaps more pleasing to have a Slater determinant in which the phase is related to the total energy. Moreover, in order to apply the variational principle of Eqs. (190) and (197) for an harmonic perturbation in the Hartree–Fock approximation it is necessary to demonstrate that the trial wave function can be written in the form of Eqs. (33) or (40). To accomplish this and in no other way alter the development resulting in Eqs. (262), we can use the arbitrariness of the Lagrangian multipliers in Eq. (253).

The appropriate choice of non-zero Langrangian multipliers is introduced by writing

$$\lambda_{ij}(t)=\lambda_i(t)\delta_{ij},\quad(268)$$

where the $\lambda_i(t)$ are arbitrary real functions of the time. With this choice we obtain from Eqs. (250) and (253)

$$[h(\mathbf{r}_i,t)+g^{(1)}(\mathbf{r}_i,t)+\lambda_i(t)-i\hbar(\partial/\partial t)]u_i'(\mathbf{r}_i,t)=0,\quad(269a)$$

$$u_i'(\mathbf{r}_i,t)=u_i(\mathbf{r}_i,t)\exp\left(-(i\hbar)^{-1}\int_{-\infty}^{t}\lambda_i(t')\,dt'\right),\quad(269b)$$

for the new orbital equation, with $u_i(\mathbf{r}_i,t)$ the solution of the canonical equation [Eq. (255)]. That is, introduction of the nonzero real Lagrangian multiplers [Eq. (268)] merely alters the spin–orbital solutions by the phase factor in Eq. (269b). Consequently, any choice of the $\lambda_i(t)$ that is real will satisfy the orthonormality conditions [Eq. (250)]. The new Hartree–Fock wave function, employing the multipliers $\lambda_i(t)$, becomes

$$\Psi_{\mathrm{HF}}(\mathbf{r},t)=(N!)^{-1/2}\det|\,\chi_1(\mathbf{r}_1,t)\chi_2(\mathbf{r}_2,t)\cdots\chi_N(\mathbf{r}_N,t)\,|\times\exp\left((i\hbar)^{-1}\sum_{i=1}^{N}\int_{-\infty}^{t}[\mathrm{Re}\,\epsilon_i(t')-\lambda_i(t')]\,dt'\right),\quad(270)$$

and clearly differs from Eq. (265) only by an over-all phase. We now choose the arbitrary real functions $\lambda_i(t)$ so that

$$\sum_{i=1}^{N}[\mathrm{Re}\,\epsilon_i(t)-\lambda_i(t)]=\langle\chi_{\mathrm{HF}}\,|\,H^{(0)}+H^{(1)}-i\hbar(\partial/\partial t)\,|\,\chi_{\mathrm{HF}}\rangle\quad(271)$$

where

$$\chi_{\mathrm{HF}}(\mathbf{r},t)=(N!)^{-1/2}\det|\,\chi_1(\mathbf{r}_1,t)\chi_2(\mathbf{r}_2,t)\cdots\chi_N(\mathbf{r}_N,t)\,|.\quad(272)$$

The complete Hartree–Fock wave function [Eq. (270)] is, therefore,

$$\Psi_{\mathrm{HF}}(\mathbf{r},t)=\chi_{\mathrm{HF}}(\mathbf{r},t)\exp\left((i\hbar)^{-1}\int_{-\infty}^{t}\langle\chi_{\mathrm{HF}}\,|\,H^{(0)}+H^{(1)}-i\hbar\frac{\partial}{\partial t}\,|\,\chi_{\mathrm{HF}}\rangle\,dt'\right)\quad(273)$$

similar to Eq. (40), where the spin–orbitals $\chi_i(\mathbf{r}_i,t)$ in Eq. (272) are given by Eqs. (260) and (266).

To complete the development, it is useful to derive a variational equation for the spin–orbitals $\phi_i^{(1)}(\mathbf{r}_i,t)$ of Eq. (262b) in the case of an harmonic perturbation. This can be accomplished by inspection of the form of Eq. (262b), although it is perhaps more instructive to follow the general development of Sec. V.A. We employ a trial Hartree–Fock wave function in the form of Eq. (273) and the variational principle of Eq. (197);

$$\delta\{J[\tilde{\chi}_{\mathrm{HF}}]\}=0,\quad(274)$$

where

$$J[\tilde{\chi}_{\mathrm{HF}}]=\langle\tilde{\chi}_{\mathrm{HF}}\,|\,H^{(0)}+H^{(1)}-i\hbar(\partial/\partial t)\,|\,\tilde{\chi}_{\mathrm{HF}}\rangle,\quad(275)$$

$$\tilde{\chi}_{\mathrm{HF}}(\mathbf{r},t)=(N!)^{-1/2}\det|\,\tilde{\chi}_1(\mathbf{r}_1,t)\,\tilde{\chi}_2(\mathbf{r}_2,t)\cdots\tilde{\chi}_N(\mathbf{r}_N,t)\,|,\quad(276)$$

and the perturbation Hamiltonian is given by Eq. (114) where the one-particle operator $g^{(1)}(\mathbf{r}_i,t)$ has an

harmonic time dependence. The appropriate form of the spin–orbital $\tilde{\chi}_i(\mathbf{r}_i, t)$, to first order, is [Eq. (266)]

$$\tilde{\chi}_i(\mathbf{r}_i, t) = \phi_i^{(0)}(\mathbf{r}_i) + \tilde{\phi}_i^{(1)}(\mathbf{r}_i, t) + \cdots, \quad (277)$$

where

$$\tilde{\phi}_i^{(1)}(\mathbf{r}_i, t) = \tilde{\phi}_{i+}^{(1)}(\mathbf{r}_i) \exp(i\omega t) + \tilde{\phi}_{i-}^{(1)}(\mathbf{r}_i) \exp(-i\omega t). \quad (278)$$

In Eq. (277), $\phi_i^{(0)}(\mathbf{r}_i)$ is the solution of Eq. (262a),[93] and the $\tilde{\phi}_{i\pm}^{(1)}(\mathbf{r}_i)$ satisfy the orthogonality requirements

$$\langle \phi_i^{(0)} \mid \tilde{\phi}_{i\pm}^{(1)} \rangle = 0 \qquad i = 1, 2, \cdots, N, \quad (279a)$$

$$\langle \tilde{\phi}_{j\pm}^{(1)} \mid \phi_i^{(0)} \rangle + \langle \phi_j^{(0)} \mid \tilde{\phi}_{i\mp}^{(1)} \rangle = 0 \qquad i, j = 1, 2, \cdots, N, \quad (279b)$$

which insure that the $\tilde{\chi}_i(\mathbf{r}_i, t)$ [Eq. (277)] are orthonormal to first order. Retaining terms through second order, we obtain from Eq. (275)

$$\{J[\tilde{\chi}_{\mathrm{HF}}]\} = E_{\mathrm{HF}}^{(0)} + \{K_{\mathrm{HF}}^{(2)}[\tilde{\chi}_{\mathrm{HF}}]\} + \cdots, \quad (280)$$

where

$$\begin{aligned}\{K_{\mathrm{HF}}^{(2)}[\tilde{\chi}_{\mathrm{HF}}]\} = \sum_{i=1}^{N} [&\langle \tilde{\phi}_{i+}^{(1)} \mid h^{(0)} - \epsilon_i^{(0)} + \hbar\omega \mid \tilde{\phi}_{i+}^{(1)} \rangle \\ &+ \langle \tilde{\phi}_{i-}^{(1)} \mid h^{(0)} - \epsilon_i^{(0)} - \hbar\omega \mid \tilde{\phi}_{i-}^{(1)} \rangle \\ &+ \langle \phi_i^{(0)} \mid h^{(1)} + \tfrac{1}{2} v_-^{(1)} \mid \tilde{\phi}_{i+}^{(1)} \rangle + \langle \tilde{\phi}_{i+}^{(1)} \mid h^{(1)} \\ &+ \tfrac{1}{2} v_+^{(1)} \mid \phi_i^{(0)} \rangle + \langle \phi_i^{(0)} \mid h^{(1)} + \tfrac{1}{2} v_+^{(1)} \mid \tilde{\phi}_{i-}^{(1)} \rangle \\ &+ \langle \tilde{\phi}_{i-}^{(1)} \mid h^{(1)} + \tfrac{1}{2} v_-^{(1)} \mid \phi_i^{(0)} \rangle], \end{aligned} \quad (281)$$

and $h^{(1)}(\mathbf{r}_i)$ is the spatial portion of the one-particle perturbation $g^{(1)}(\mathbf{r}_i, t)$ [Eq. (114)]. In Eq. (281) we have introduced the first-order self-consistent potentials

$$\begin{aligned} v_\pm^{(1)}(\mathbf{r}_i) = \sum_{j=1}^{N} (&\langle \tilde{\phi}_{j\mp}^{(1)} \mid (e^2/r_{ij})(1 - P_{ij}) \mid \phi_j^{(0)} \rangle \\ &+ \langle \phi_j^{(0)} \mid (e^2/r_{ij})(1 - P_{ij}) \mid \tilde{\phi}_{j\pm}^{(1)} \rangle), \end{aligned} \quad (282)$$

which clearly depend on the unknown solutions $\tilde{\phi}_{i\pm}^{(1)}(\mathbf{r}_i)$. The functional of Eq. (281) is made stationary with respect to variations of all the trial spin–orbitals $\tilde{\phi}_{i\pm}^{(1)}(\mathbf{r}_i)$ [Eq. (274)], subject to the orthogonality requirements of Eqs. (279). We note that the canonical choice of Lagrangian multipliers

$$\lambda_{ij}(\pm)^{(1)} = \lambda_{i\pm}^{(1)} \delta_{ij} \quad (283)$$

can be employed to satisfy Eqs. (279) since, as we shall see, they will be satisfied automatically as a consequence of the resulting differential equations for $\tilde{\phi}_{i\pm}^{(1)}(\mathbf{r}_i)$. Introducing the multipliers [Eq. (283)], we obtain from Eqs. (274) and (281) the variational equations

$$\begin{aligned}\delta[\{K_{\mathrm{HF}}^{(2)}[\tilde{\chi}_{\mathrm{HF}}]\} + \sum_{i=1}^{N} &(\lambda_{i+}^{(1)} \langle \tilde{\phi}_{i+}^{(1)} \mid \phi_i^{(0)} \rangle \\ &+ (\lambda_{i+}^{(1)})^* \langle \phi_i^{(0)} \mid \tilde{\phi}_{i+}^{(1)} \rangle + \lambda_{i-}^{(1)} \langle \tilde{\phi}_{i-}^{(1)} \mid \phi_i^{(0)} \rangle \\ &+ (\lambda_{i-}^{(1)})^* \langle \phi_i^{(0)} \mid \tilde{\phi}_{i-}^{(1)} \rangle)] = 0. \end{aligned} \quad (284)$$

Carrying out the indicated variations gives the differential equations

$$\begin{aligned}[h^{(0)}(\mathbf{r}_i) - \epsilon_i^{(0)} \pm \hbar\omega] \tilde{\phi}_{i\pm}^{(1)}(\mathbf{r}_i) \\ + [h^{(1)}(\mathbf{r}_i) + v_\pm^{(1)}(\mathbf{r}_i) + \lambda_{i\pm}^{(1)}] \phi_i^{(0)}(\mathbf{r}_i) = 0 \end{aligned} \quad (285)$$

and from the requirement that Eq. (279a) be satisfied at the solution point, we find

$$\lambda_{i\pm}^{(1)} = -\langle \phi_i^{(0)} \mid h^{(1)} + v_\pm^{(1)} \mid \phi_i^{(0)} \rangle. \quad (286)$$

We see that Eq. (279b) is an immediate consequence of Eqs. (285) and (286) and, consequently, the canonical choice of multipliers [Eq. (283)] is satisfactory, involving no loss of generality. Equations (285) and (286) are identical with Eq. (262b) in the case of an harmonic perturbation, for which Eq. (278) is appropriate. Consequently, we have obtained a variational formulation of the first-order time-dependent Hartree–Fock equations for the regular part of the spin–orbital in the form of the functional in Eqs. (284) and (286).

At the solution point we find

$$\begin{aligned}\epsilon_{\mathrm{HF}}^{(2)} = \{K_{\mathrm{HF}}^{(2)}[\chi_{\mathrm{HF}}]\} = \sum_{i=1}^{N} (&\langle \phi_i^{(0)} \mid h^{(1)} \mid \phi_{i+}^{(1)} \rangle \\ &+ \langle \phi_{i-}^{(1)} \mid h^{(1)} \mid \phi_i^{(0)} \rangle) \end{aligned} \quad (287)$$

similar to the result of Eq. (247). Here, however, the first-order spin–orbitals are determined from the coupled Hartree–Fock equations, whereas the uncoupled Hartree–Fock spin-orbitals are employed in Eq. (247). From the second variation of the functional [Eq. (281)] at the solution point we have

$$\{K_{\mathrm{HF}}^{(2)}[\tilde{\chi}_{\mathrm{HF}}]\} \geq \{K_{\mathrm{HF}}^{(2)}[\chi_{\mathrm{HF}}]\} = \epsilon_{\mathrm{HF}}^{(2)} \qquad \omega < \omega_{10}, \quad (288)$$

where $\omega_{10}$ is the coupled Hartree–Fock resonance frequency and, consequently, a bounded variational

[93] Accurate solutions of Eq. (262a) can be obtained for atoms and ions but only approximate variational solutions, which do not satisfy Eq. (262a), are available for molecules. In the latter case an alternative variational formulation of the first-order Hartree–Fock equations, which does not assume that Eq. (262a) is satisfied, can be carried out, although we do not consider this case explicitly here. A formalism similar to that of Lipscomb (1969) is conveniently employed.

principle for the coupled Hartree–Fock approximation to the second-order level shift is obtained.[94]

## VI. CONCLUDING REMARKS

In this review we have drawn attention to the presence of normalization and secular terms in the Dirac variation-of-constants perturbative solution of the time-dependent Schrödinger equation. While the Dirac solutions are perfectly correct and do not result in formal difficulties, it is nevertheless convenient and instructive to isolate the normalization and secular terms that arise into over-all multiplicative normalization and phase factors, and to employ the remaining regular part of the wave function in perturbation or variational developments. The extraction of the secular terms into an over-all phase factor is particularly important when the perturbed system exhibits a physically significant level shift. Since it is difficult to extract the individual secular and normalization terms from the wave function on an order-by-order basis, we have employed a method for extracting them once and for all to all orders in perturbation theory, and have demonstrated that the resulting normalization and phase factors are determined by the regular part of the wave function. It is the power series expansions of the normalization and phase factors, combined with the perturbation expansion of the regular function itself, that give rise to the customary Dirac variation-of-constants perturbative solutions. The perturbation expansion of the regular function results in a sequence of equations that bear strong resemblance to the time-independent perturbation equations and reduce to the latter in the static limit. This contrasts with the Dirac expansion, where the static limit is somewhat obscured.

Our applications in the cases of the linearly perturbed oscillator, for which the exact wave function is obtained, and the static, harmonic, and electromagnetic perturbations, where approximate perturbative solutions are obtained, serve to emphasize that the procedure we have followed is essentially one of regrouping the Dirac solutions in a form that makes apparent the presence of over-all normalization and phase factors. In the case of an adiabatically applied harmonic perturbation, the over-all multiplicative phase factor obtained includes both oscillatory terms and terms linear in the time that describes the system level shift in the presence of an oscillating field. In the limit of a static perturbation, the over-all phase factor reduces to the customary static level shift factor, in agreement with the well-known adiabatic theorem. By contrast, the Dirac functions, which include the perturbative expansion of the level shift factor, contain time diverging secular terms in the case of an adiabatically applied static perturbation.

The relative simplicity enjoyed by the use of the regular functions, in contrast to the Dirac expansion, is clearly exhibited by the compact expressions we have obtained for various nonlinear optical susceptibilities. Our treatments of the uncoupled and coupled time-dependent Hartree–Fock approximations have also illustrated the importance and convenience of computing only the regular portion of the wave function and underline some of the possible pitfalls encountered when normalization or secular terms are retained.

Methods other than our simple extraction procedure can also be employed for eliminating normalization and secular terms from the wave function. We have considered a projection procedure and methods of extention and averaging familiar from nonlinear mechanics and nonequilibrium statistical mechanics. In contrast to the latter problems, where the long time behavior of the system is the essential element, the presence of secular terms in quantum mechanics offers no fundamental formal difficulties and they can perhaps be most conveniently treated by our simple extraction procedure. In the Fourier analysis of a general time-dependent perturbation, we have noted that the extraction of secular terms from the wave function is necessary to insure that a valid Fourier transform is obtained.

Finally, in considering the variational formulation of time-dependent perturbation theory, we have found it of the utmost importance to employ the regular portion of the wave function. By writing a trial wave function in a form which explicitly exhibits the normalization and secular terms, we have shown that the Frenkel variational principle provides a computationally convenient functional which can provide a bound on the system level shift induced by an oscillatory perturbation. This form of the Frenkel principle furnishes a unification of previously described order-by-order variational techniques and reduces to the familiar Ritz principle in the static limit.

In conclusion, the Dirac variation-of-constants method and the Frenkel variational principle, when properly interpreted and applied, provide correct and convenient solutions of the time-dependent Schrödinger equation. It is of considerable importance, however, to deal carefully with the secular and normalization terms in order to avoid spurious difficulties in the use of these techniques.

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[94] The coupled Hartree–Fock approximation has been employed in a variety of computational determinations of the dynamic polarizabilities and related excitation spectra of simple atoms and molecules. See, for example, Altick and Glassgold (1964), Dalgarno and Victor (1966), Sengupta and Mukherji (1967), Victor (1967), Dunning and McKoy (1967, 1968), Kaveeshwar, Chung, and Hurst (1968), Mukerjee, Sengupta, and Mukherji (1969), Epstein (1970), Epstein and Lipscomb (1970), Jørgensen and Linderberg (1970), Langhoff and Karplus (1970a), Moitra, Mukherjee, and Sengupta (1970), Jamison (1971), Bhattacharya, Sengupta, and Mukherji (1972), and Moitra and Mukherjee (1972).

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## VII. APPENDIX

### A. Wave Functions in an Oscillating Field

The solutions of Eqs. (88) for the spatial portions of the perturbation functions [Eqs. (87) and (91)] in an oscillating field can be written in terms of the spectral expansions,

$$\phi_{\pm 1}^{(1)}(\mathbf{r}) = \sum_{k\neq 0}^{\infty} b_k^{(1)}(\pm 1)\phi_k^{(0)}(\mathbf{r}), \tag{A1}$$

$$\phi_{\pm 2}^{(2)}(\mathbf{r}) = \sum_{k\neq 0}^{\infty} b_k^{(2)}(\pm 2)\phi_k^{(0)}(\mathbf{r}), \tag{A2}$$

$$\phi_0^{(2)}(\mathbf{r}) = \sum_{k\neq 0}^{\infty} b_k^{(2)}(0)\phi_k^{(0)}(\mathbf{r}), \tag{A3}$$

$$\phi_{\pm 3}^{(3)}(\mathbf{r}) = \sum_{k\neq 0}^{\infty} b_k^{(3)}(\pm 3)\phi_k^{(0)}(\mathbf{r}), \tag{A4}$$

$$\phi_{\pm 1}^{(3)}(\mathbf{r}) = \sum_{k\neq 0}^{\infty} b_k^{(3)}(\pm 1)\phi_k^{(0)}(\mathbf{r}). \tag{A5}$$

Employing the notation,

$$h_{kl}^{(1)} = \hbar^{-1}\langle \phi_k^{(0)} \mid h^{(1)} \mid \phi_l^{(0)} \rangle, \tag{A6}$$

$$\omega_{k_0} = \hbar^{-1}(E_k^{(0)} - E_0^{(0)}), \tag{A7}$$

we find

$$b_k^{(1)}(\pm 1) = -h_{k0}^{(1)}(\omega_{k0}\pm\omega)^{-1}, \tag{A8}$$

$$b_k^{(2)}(\pm 2) = -h_{k0}^{(1)}h_{00}^{(1)}(\omega_{k0}\pm 2\omega)^{-1}(\omega_{k0}\pm\omega)^{-1} + \sum_{l\neq 0}^{\infty}\{h_{kl}^{(1)}h_{l0}^{(1)}(\omega_{k0}\pm 2\omega)^{-1}(\omega_{l0}\pm\omega)^{-1}\}, \tag{A9}$$

$$b_k^{(2)}(0) = -2h_{k0}^{(1)}h_{00}^{(1)}(\omega_{k0}^2-\omega^2)^{-1} + \sum_{l\neq 0}^{\infty}\{2h_{kl}^{(1)}h_{l0}^{(1)}\omega_{l0}\omega_{k0}^{-1}(\omega_{l0}^2-\omega^2)^{-1}\}, \tag{A10}$$

$$\begin{aligned} b_k^{(3)}(\pm 3) = &-h_{k0}^{(1)}h_{00}^{(1)}h_{00}^{(1)}(\omega_{k0}\pm 3\omega)^{-1}(\omega_{k0}\pm 2\omega)^{-1}(\omega_{k0}\pm\omega)^{-1} + \sum_{l\neq 0}^{\infty}\{h_{k0}^{(1)}h_{0l}^{(1)}h_{l0}^{(1)}(\omega_{k0}\pm 3\omega)^{-1}(\omega_{k0}\pm\omega)^{-1}(\omega_{l0}\pm\omega)^{-1} \\ &+h_{kl}^{(1)}h_{l0}^{(1)}h_{00}^{(1)}(\omega_{l0}+\omega_{k0}\pm 4\omega)(\omega_{k0}\pm 3\omega)^{-1}(\omega_{k0}\pm 2\omega)^{-1}(\omega_{l0}\pm 2\omega)^{-1}(\omega_{l0}\pm\omega)^{-1}\} \\ &-\sum_{l\neq 0}^{\infty}\sum_{m\neq 0}^{\infty}\{h_{kl}^{(1)}h_{lm}^{(1)}h_{m0}^{(1)}(\omega_{k0}\pm 3\omega)^{-1}(\omega_{l0}\pm 2\omega)^{-1}(\omega_{m0}\pm\omega)^{-1}\}, \end{aligned} \tag{A11}$$

$$\begin{aligned} b_k^{(3)}(\pm 1) = &-h_{k0}^{(1)}h_{00}^{(1)}h_{00}^{(1)}[2(\omega_{k0}\pm\omega)^{-1}(\omega_{k0}^2-\omega^2)^{-1} + (\omega_{k0}\pm\omega)^{-2}(\omega_{k0}\pm 2\omega)^{-1}] \\ &+\sum_{l\neq 0}^{\infty}\{h_{kl}^{(1)}h_{l0}^{(1)}h_{00}^{(1)}[(\omega_{k0}+\omega_{l0}\pm 4\omega)(\omega_{k0}\pm 2\omega)^{-1}(\omega_{l0}\pm 2\omega)^{-1}(\omega_{k0}\pm\omega)^{-1}(\omega_{l0}\pm\omega)^{-1} \\ &+2(1+\omega_{l0}\omega_{k0}^{-1})(\omega_{k0}\pm\omega)^{-1}(\omega_{l0}^2-\omega^2)^{-1}] + h_{k0}^{(1)}h_{0l}^{(1)}h_{l0}^{(1)}[2\omega_{l0}(\omega_{k0}\pm\omega)^{-2}(\omega_{l0}^2-\omega^2)^{-1} + (\omega_{l0}\pm\omega)^{-1}(\omega_{k0}^2-\omega^2)^{-1}]\} \\ &-\sum_{l\neq 0}^{\infty}\sum_{m\neq 0}^{\infty}\{h_{kl}^{(1)}h_{lm}^{(1)}h_{m0}^{(1)}(\omega_{k0}\pm\omega)^{-1}[2\omega_{m0}\omega_{l0}^{-1}(\omega_{m0}^2-\omega^2)^{-1} + (\omega_{m0}\pm\omega)^{-1}(\omega_{l0}\pm 2\omega)^{-1}]\}. \end{aligned} \tag{A12}$$

### B. Nonlinear Optical Susceptibilities

The wave functions of Appendix A are employed in the susceptibilities of Eqs. (105) to obtain expressions in terms of spectral sums over virtual intermediate states. In the uniform-electric-field approximation, the perturbation operator appearing in the matrix elements $h_{kl}^{(1)}$ of Appendix A is given by [Eq. (102b)]

$$h^{(1)}(\mathbf{r}) = -e\mathbf{r}\cdot\mathbf{a}, \tag{B1}$$

with $\mathbf{a}$ the polarization vector, and we introduce the notation,

$$\mathbf{r}_{kl} = \langle \phi_k^{(0)} \mid \mathbf{r} \mid \phi_l^{(0)} \rangle, \tag{B2}$$

for the matrix elements of the dipole moment operator. Employing Eqs. (B1) and (B2), and the convention that the notation $\pm$ implies summation over both $+$ and $-$ terms, we obtain

$$\mathbf{P}_\omega^{(1)} = -\sum_{k\neq 0}^{\infty} \{\mathbf{r}_{k0} h_{k0}^{(1)} (\omega_{k0} \pm \omega)^{-1}\}, \tag{B3}$$

$$\mathbf{P}_0^{(2)} = -(1/4)\sum_{k\neq 0}^{\infty} \{2\mathbf{r}_{0k} h_{k0}^{(1)} h_{00}^{(1)} \omega_{k0}^{-1} (\omega_{k0} \pm \omega)^{-1} + \mathbf{r}_{00} h_{0k}^{(1)} h_{k0}^{(1)} (\omega_{k0} \pm \omega)^{-2}\}$$

$$+ (1/4)\sum_{k\neq 0}^{\infty}\sum_{l\neq 0}^{\infty} \{2\mathbf{r}_{0k} h_{kl}^{(1)} h_{l0}^{(1)} \omega_{k0}^{-1} (\omega_{l0} \pm \omega)^{-1} + h_{0k}^{(1)} \mathbf{r}_{kl} h_{l0}^{(1)} (\omega_{k0} \pm \omega)^{-1} (\omega_{l0} \pm \omega)^{-1}\}, \tag{B4}$$

$$\mathbf{P}_{2\omega}^{(2)} = -(1/2)\sum_{k\neq 0}^{\infty} \{\mathbf{r}_{0k} h_{k0}^{(1)} h_{00}^{(1)} (\omega_{k0} \pm 2\omega)^{-1} (\omega_{k0} \pm \omega)^{-1} + \mathbf{r}_{00} h_{0k}^{(1)} h_{k0}^{(1)} (\omega_{k0}^2 - \omega^2)^{-1}\}$$

$$+ (1/2)\sum_{k\neq 0}^{\infty}\sum_{l\neq 0}^{\infty} \{\mathbf{r}_{0k} h_{kl}^{(1)} h_{l0}^{(1)} (\omega_{k0} \pm 2\omega)^{-1} (\omega_{l0} \pm \omega)^{-1} + h_{0k}^{(1)} \mathbf{r}_{kl} h_{l0}^{(1)} (\omega_{k0} + \omega)^{-1} (\omega_{l0} - \omega)^{-1}\}, \tag{B5}$$

$$\begin{aligned}
\mathbf{P}_\omega^{(3)} = &-(1/4)\sum_{k\neq 0}^{\infty} \{[\mathbf{r}_{0k} h_{k0}^{(1)} h_{00}^{(1)} + \mathbf{r}_{00} h_{0k}^{(1)} h_{k0}^{(1)} h_{00}^{(1)}][2(\omega_{k0} \pm \omega)^{-1} (\omega_{k0}^2 - \omega^2)^{-1} + (\omega_{k0} \pm \omega)^{-2} (\omega_{k0} \pm 2\omega)^{-1}]\} \\
&+ (1/4)\sum_{k\neq 0}^{\infty}\sum_{l\neq 0}^{\infty} \{\mathbf{r}_{00} h_{0k}^{(1)} h_{kl}^{(1)} h_{l0}^{(1)} [(\omega_{k0} \pm \omega)^{-1} (\omega_{k0} \pm 2\omega)^{-1} (\omega_{l0} \pm \omega)^{-1} + 2\omega_{l0}\omega_{k0}^{-1} (\omega_{k0} \pm \omega)^{-1} (\omega_{l0}^2 - \omega^2)^{-1}] \\
&\quad + h_{0k}^{(1)} \mathbf{r}_{kl} h_{l0}^{(1)} h_{00}^{(1)} [(\omega_{k0} \pm \omega)^{-1} (\omega_{l0} \pm 2\omega)^{-1} (\omega_{l0} \pm \omega)^{-1} + 2(\omega_{k0} \pm \omega)^{-1} (\omega_{l0}^2 - \omega^2)^{-1}] \\
&\quad + \mathbf{r}_{0k} h_{kl}^{(1)} h_{l0}^{(1)} h_{00}^{(1)} [(\omega_{k0} + \omega_{l0} \pm 4\omega)(\omega_{k0} \pm 2\omega)^{-1} (\omega_{l0} \pm 2\omega)^{-1} (\omega_{k0} \pm \omega)^{-1} (\omega_{l0} \pm \omega)^{-1} \\
&\quad + 2(1 + \omega_{l0}\omega_{k0}^{-1})(\omega_{k0} \pm \omega)^{-1} (\omega_{l0}^2 - \omega^2)^{-1}] + \mathbf{r}_{0k} h_{k0}^{(1)} h_{0l}^{(1)} h_{l0}^{(1)} [2\omega_{l0}(\omega_{k0} \pm \omega)^{-2} (\omega_{l0}^2 - \omega^2)^{-1} \\
&\quad + (\omega_{l0} \pm \omega)^{-1} (\omega_{k0}^2 - \omega^2)^{-1} + 2\omega_{k0}(\omega_{k0}^2 - \omega^2)^{-1} (\omega_{l0}^2 - \omega^2)^{-1} + 2\omega_{k0}(\omega_{k0}^2 - \omega^2)^{-1} (\omega_{l0} \pm \omega)^{-2}]\} \\
&- (1/4)\sum_{k\neq 0}^{\infty}\sum_{l\neq 0}^{\infty}\sum_{m\neq 0}^{\infty} \{[\mathbf{r}_{0k} h_{kl}^{(1)} h_{lm}^{(1)} h_{m0}^{(1)} + h_{0k}^{(1)} \mathbf{r}_{kl} h_{lm}^{(1)} h_{m0}^{(1)}][(\omega_{k0} \pm \omega)^{-1} (\omega_{l0} \pm 2\omega)^{-1} (\omega_{m0} \pm \omega)^{-1} \\
&\quad + 2(\omega_{k0} \pm \omega)^{-1} \omega_{m0}\omega_{l0}^{-1} (\omega_{m0}^2 - \omega^2)^{-1}]\},
\end{aligned} \tag{B6}$$

$$\begin{aligned}
\mathbf{P}_{3\omega}^{(3)} = &-(1/4)\sum_{k\neq 0}^{\infty} \{\mathbf{r}_{0k} h_{k0}^{(1)} h_{00}^{(1)} h_{00}^{(1)} (\omega_{k0} \pm 3\omega)^{-1} (\omega_{k0} \pm 2\omega)^{-1} (\omega_{k0} \pm \omega)^{-1} \\
&\quad + \mathbf{r}_{00} h_{0k}^{(1)} h_{k0}^{(1)} h_{00}^{(1)} (\omega_{k0} \pm \omega)^{-1} (\omega_{k0} \mp 2\omega)^{-1} (\omega_{k0} \mp \omega)^{-1}\} \\
&+ (1/4)\sum_{k\neq 0}^{\infty}\sum_{l\neq 0}^{\infty} \{\mathbf{r}_{00} h_{0k}^{(1)} h_{kl}^{(1)} h_{l0}^{(1)} (\omega_{k0} \pm 2\omega)^{-1} (\omega_{k0} \mp 2\omega)^{-1} (\omega_{l0} \mp \omega)^{-1} + h_{00}^{(1)} h_{0k}^{(1)} \mathbf{r}_{kl} h_{l0}^{(1)} (\omega_{k0} \mp \omega)^{-1} (\omega_{l0} \pm 2\omega)^{-1} (\omega_{l0} \pm \omega)^{-1} \\
&\quad + \mathbf{r}_{0k} h_{k0}^{(1)} h_{0l}^{(1)} h_{l0}^{(1)} [(\omega_{k0} \pm 3\omega)^{-1} (\omega_{k0} \pm \omega)^{-1} (\omega_{l0} \pm \omega)^{-1} + 2\omega_{k0}(\omega_{k0}^2 - \omega^2)^{-1} (\omega_{l0}^2 - \omega^2)^{-1}] \\
&\quad + h_{00}^{(1)} \mathbf{r}_{0k} h_{kl}^{(1)} h_{l0}^{(1)} [(\omega_{k0} \pm 3\omega)^{-1} (\omega_{k0} \pm 2\omega)^{-1} (\omega_{l0} \pm \omega)^{-1} + (\omega_{k0} \pm 3\omega)^{-1} (\omega_{l0} \pm 2\omega)^{-1} (\omega_{l0} \pm \omega)^{-1}]\} \\
&- (1/4)\sum_{k\neq 0}^{\infty}\sum_{l\neq 0}^{\infty}\sum_{m\neq 0}^{\infty} \{\mathbf{r}_{0k} h_{kl}^{(1)} h_{lm}^{(1)} h_{m0}^{(1)} (\omega_{k0} \pm 3\omega)^{-1} (\omega_{l0} \pm 2\omega)^{-1} (\omega_{m0} \pm \omega)^{-1} \\
&\quad + h_{0k}^{(1)} \mathbf{r}_{kl} h_{lm}^{(1)} h_{m0}^{(1)} (\omega_{k0} \pm \omega)^{-1} (\omega_{l0} \mp 2\omega)^{-1} (\omega_{m0} \mp \omega)^{-1}\}.
\end{aligned} \tag{B7}$$

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