Time-Dependent Hartree–Fock Theory for Molecules

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1. INTRODUCTION

It is often useful to look at a quantum-mechanical problem from both a time-dependent and a stationary-state point of view. When a molecule absorbs radiation, for example, and its electrons are excited from the ground state there is a time-dependent problem, since the energy is absorbed when a periodic electric or magnetic field of a definite frequency acts on the molecule and sets the electrons oscillating. The solution of the time-dependent Schrödinger equation by first-order perturbation theory shows that the oscillations are small except at the "resonant" frequencies where a transition to an excited state takes place, and one could infer these frequencies, and the intensities of the absorption lines from a solution of the time-dependent equations. Usually, however, one thinks of the transitions between a set of stationary states with known energies and wave functions. Both points of view are precisely equivalent in theory, but in practice, because electron correlation has important effects on the wave functions of both ground and excited states, it is hard to estimate energies or intensities accurately in the stationary-state approach.

The time-dependent self-consistent field theory is an attempt to find an approximate solution of the time-dependent Schrödinger equation and describes the absorption of radiation in another way. The periodic electric field of the light wave sets all the electrons oscillating, each one in the average field of all the others. The Coulomb and exchange forces on each electron vary with time, but apart from this each electron moves independently of the rest, so that electron correlation effects are allowed for in a crude but simple way. At certain frequencies the coupled oscillations have "resonances" which correspond to excited states. The amplitude of the resonance then determines the oscillator strength and other properties of the transition. This sort of argument suggests that the time-dependent Hartree–Fock theory can be a useful alternative approach to molecular problems, and give a new physical description of electron correlation effects, including correlations in the ground state itself.

A time-dependent point of view is also useful in other ways. For instance in Kubo and Tomita's[1] theory of nuclear magnetic relaxation the line shape of a resonance depends on the correlation in time of the fluctuations of the nuclear spin in the ground state of the sample. In the theory of van der Waals dispersion forces the interaction energy of two molecules comes out in terms of their frequency-dependent electric polarizabilities,[2] and the force between two large bodies depends similarly on their dielectric constants at all frequencies, or simply their absorption spectra.[3] In this paper we show that the pair-correlation function of the electrons in a molecule in its ground state can be deduced from a generalized polarizability,[4] and calculate the polarizability approximately by the time-dependent Hartree–Fock method. We can also estimate part of the correlation energy directly from the Hartree–Fock "resonance frequencies" and use an analogy between the oscillations of the electrons and a set of coupled harmonic oscillators[5] which we have already found useful for discussing dispersion energies.[6] The correlation energy is closely connected with the zero-point energy of the equivalent oscillators.

Most of the ideas we use are not very new—Dirac[7] derived the time-dependent Hartree–Fock equations in 1930—but they have been elaborated recently in theories of the dielectric constant of electrons in metals,[8,9] collective motion in the electron gas,[4,10,11] and the rotational and vibrational levels of nuclei.[12–14] In these theories the method is usually called the random-phase approximation. This paper is then largely a description of what other people have done. Our aim is to present the general theorems here as clearly as possible and discuss particular applications in another paper. We have thought it worth while to do this because the method has not been applied before to molecules, and the important results are scattered in a large number of papers on different topics.

The main argument is presented in Secs. 2–6. We begin with the definitions of density operators and polarizabilities, and show how they are connected with

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[1] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

[2] A. D. McLachlan, Proc. Roy. Soc. (London) A **271**, 387 (1963).

[3] E. M. Lifshitz, Zh. Eksperim. i Teor. Fiz. **29**, 94 (1955) [English transl.: Soviet Phys.—JETP **2**, 73 (1956)].

[4] P. Nozières and D. Pines, Nuovo Cimento **9**, 470 (1958).

[5] K. Sawada, Phys. Rev. **106**, 372 (1957).

[6] A. D. McLachlan, R. D. Gregory, and M. A. Ball, Mol. Phys. **7**, 119 (1963).

[7] P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930).

[8] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. **28**, No. 8 (1954).

[9] H. Ehrenreich and M. H. Cohen, Phys. Rev. **115**, 786 (1959).

[10] J. Goldstone and K. Gottfried, Nuovo Cimento **13**, 849 (1959).

[11] R. A. Ferrell, Phys. Rev. **107**, 450 (1957).

[12] D. J. Thouless, Nucl. Phys. **21**, 225 (1960).

[13] G. E. Brown, J. A. Evans, and D. J. Thouless, Nucl. Phys. **24**, 1 (1961).

[14] R. A. Ferrell, Phys. Rev. **107**, 1631 (1957).

the correlation energy (Secs. 2–3). The time-dependent Hartree–Fock equations are introduced and used to calculate the polarizability, either directly (Sec. 4) or from the "free oscillations" of the Hartree–Fock orbitals (Sec. 5). The polarizability depends on a set of vectors which obey unusual orthogonality conditions, and the excitation frequencies are the eigenvalues of a non-Hermitian matrix. They are only real if the Hartree–Fock wave function of the ground state represents a true minimum of the energy. Finally (Sec. 6) comes the connection between zero-point energy and correlation energy.

The second half of the paper fills in some details including the derivation of the Hartree–Fock equations from a variational principle (Sec. 8) or from an operator equation of motion for the density matrix (Sec. 13), and discusses several theorems which are useful in applications of the method. They are concerned with spin effects, stability conditions, sum rules, and a transformation which connects the oscillations with the eigenvectors of a *Hermitian* matrix.

2. PAIR CORRELATIONS AND POLARIZABILITY

In this section we use the creation and destruction operators $\eta_a{}^*$, $\eta_b{}^*$, $\cdots\eta_a$, η_b, $\cdots$ which act on electrons in a complete set of orthonormal spin-orbitals ψ_a, ψ_b, $\cdots$.[15,16] The Hamiltonian consists of the kinetic and potential energy U in the field of the fixed nuclei and the Coulomb interaction G between the electrons, and takes the form

$$\hat{H}=\sum_{a,b}\eta_b{}^*\eta_a U_{ba}+\tfrac{1}{2}\sum_{a,b,c,d}\eta_c{}^*\eta_d{}^*\eta_b\eta_a\langle cd\mid G\mid ab\rangle. \qquad (2.1)$$

We also introduce one-electron and two-electron density operators

$$\hat{\rho}_{ab}=\eta_b{}^*\eta_a, \qquad \hat{\rho}_{ab:cd}=\eta_c{}^*\eta_d{}^*\eta_b\eta_a. \qquad (2.2)$$

Their mean values in any state are the corresponding components of the one and two-particle density matrices ρ_{ab} and $\rho_{ab:cd}$ of the electrons

$$\rho_{ab}=\langle\hat{\rho}_{ab}\rangle, \qquad \rho_{ab:cd}=\langle\hat{\rho}_{ab:cd}\rangle, \qquad (2.3)$$

and in this notation the Hamiltonian becomes

$$\hat{H}=\hat{\rho}_{ab}U_{ba}+\tfrac{1}{2}\hat{\rho}_{ab:cd}\langle cd\mid G\mid ab\rangle \qquad (2.4)$$

while the usual Dirac density matrix is

$$\rho(q,q')=\rho_{ab}\psi_a(q)\psi_b{}^*(q'). \qquad (2.5)$$

(From now on we use the summation convention for repeated suffices in all equations).

When any small perturbation of the type

$$-\hat{f}(t)=-\hat{\rho}_{ab}f_{ba}(t), \qquad (2.6)$$

with $\hat{f}$ an arbitrary one-electron operator, acts on the electrons it induces small changes in the density which are described by a linear-response function $K(\tau)$[17]

$$\rho_{ab}(t)-\rho_{ab}(0)=\int_0^\infty K_{ab:cd}(\tau)f_{dc}(t-\tau)\,d\tau. \qquad (2.7)$$

First-order perturbation theory[1] shows that

$$K_{ab:cd}(\tau)=(i/\hbar)\langle[\hat{\rho}_{ab}(\tau),\hat{\rho}_{cd}(0)]\rangle, \qquad (2.8)$$

so the response function is the average value in the unperturbed ground state of the molecule of the commutator of the Heisenberg operators $\hat{\rho}_{ab}(\tau)$ and $\hat{\rho}_{cd}(0)$.

When the forces are resolved into Fourier components $f_{ba}(\omega)$ with time factors $e^{-i\omega t}$ the mean value of $\hat{\rho}_{ab}$ has components

$$\rho_{ab}(\omega)=A_{ab:cd}(\omega)f_{dc}(\omega), \qquad (2.9)$$

where $A(\omega)$, the generalized polarizability, is the Fourier transform of $K(\tau)$. $A(\omega)$ splits up into Hermitian and anti-Hermitian parts which give rise to dispersion and absorption

$$A(\omega)=A'(\omega)+iA''(\omega). \qquad (2.10)$$

Since the operators $\hat{\rho}_{ab}$ are not Hermitian, but $(\hat{\rho}_{ab})_{0n}{}^*=(\hat{\rho}_{ba})_{n0}$, the part A' is not Hermitian in the usual sense, but $A'_{ab:cd}{}^*(\omega)=A'_{dc:ba}(\omega)$. It is useful to express A' and A'' in terms of the "transition electron densities" between the exact stationary states.

$$A'_{ab:cd}(\omega)=\frac{P}{\hbar}\sum_n\left\{\frac{(\hat{\rho}_{ab})_{0n}(\hat{\rho}_{cd})_{n0}}{\omega_{n0}-\omega}+\frac{(\hat{\rho}_{cd})_{0n}(\hat{\rho}_{ab})_{n0}}{\omega_{n0}+\omega}\right\} \qquad (2.11)$$

$$A''_{ab:cd}(\omega)=\frac{\pi}{\hbar}\sum_n\{(\hat{\rho}_{ab})_{0n}(\hat{\rho}_{cd})_{n0}\delta(\omega-\omega_{n0})$$
$$-(\hat{\rho}_{cd})_{0n}(\hat{\rho}_{ab})_{n0}\delta(\omega+\omega_{n0})\}. \qquad (2.12)$$

Here P stands for the principal value as ω approaches the poles of $A'(\omega)$ at $\pm\omega_{n0}$, and the sum does not include the ground state.

We can infer the pair-correlation function from the polarizability.[4] The commutation laws of the $\eta_a{}^*$, η_a operators give an operator relation between the one and two-particle density *operators*

$$\hat{\rho}_{ab:cd}=\hat{\rho}_{ac}\hat{\rho}_{bd}-\delta_{ad}\hat{\rho}_{bc}=\hat{\rho}_{bd}\hat{\rho}_{ac}-\delta_{bc}\hat{\rho}_{ad}, \qquad (2.13)$$

and then matrix multiplication gives the identity

$$\rho_{ab:cd}=\rho_{ac}\rho_{bd}-\delta_{ad}\rho_{bc}+\sum_n(\rho_{ac})_{0n}(\rho_{bd})_{n0} \qquad (2.14)$$

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[15] P. A. M. Dirac, *Quantum Mechanics* (Clarendon Press, Oxford, England, 1958), 4th ed.

[16] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press, Inc., London, 1958).

[17] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Inc., London, 1958).

for the mean value in the ground state. This takes a more familiar form if $\rho(\mathbf{r}_1)$ is the ordinary electron density in space, and $\sigma(\mathbf{r}_1, \mathbf{r}_2)$ is the pair-correlation function:

$$\sigma(\mathbf{r}_1, \mathbf{r}_2)=\rho(\mathbf{r}_1)\rho(\mathbf{r}_2) -\delta(\mathbf{r}_1-\mathbf{r}_2)\rho(\mathbf{r}_1)+\sum_n \rho(\mathbf{r}_1)_{0n}\rho(\mathbf{r}_2)_{n0}. \quad (2.15)$$

The polarizability obeys a sum rule derived from (2.12)

$$\frac{\hbar}{\pi}\int_0^\infty A''_{ab:cd}(\omega)\,d\omega=\sum_n(\rho_{ab})_{0n}(\rho_{cd})_{n0}=I_{ab:cd}, \quad (2.16)$$

and so the two-particle density matrix becomes

$$\rho_{ab:cd}=\rho_{ac}\rho_{bd}-\delta_{ad}\rho_{bc}+I_{ac:bd}. \quad (2.17)$$

This result is exact, but its value depends on how well we can estimate the polarizability.

3. SEPARATION OF THE HAMILTONIAN

The first approximation to the wave function is the Hartree–Fock single determinant

$$\Phi_0=\|\psi_1\cdots\psi_m\cdots\psi_N\| \quad (3.1)$$

in which occupied spin orbitals are labeled $m, n, \cdots$, vacant ones $j, k, \cdots$ and all satisfy the Hartree–Fock equations

$$F\psi_i=\epsilon_i\psi_i. \quad (3.2)$$

F is the one-electron operator defined by its matrix elements

$$F_{ab}=U_{ab}+\sum_m^{\text{occ}}\langle am \mid bm\rangle \quad (3.3)$$

and we have introduced antisymmetrized electron repulsion integrals

$$\langle ab \mid cd\rangle=\langle ab \mid G \mid cd\rangle-\langle ab \mid G \mid dc\rangle. \quad (3.4)$$

The complete set $a, b, c, \cdots$ are now taken to be the Hartree–Fock orbitals.

In this approximation the excitation energy for a single electron jump is $(\epsilon_k-\epsilon_m)$ and the polarizability $\alpha(\omega)$ has only two nonvanishing components

$$\alpha_{mk:km}=1/\hbar(\omega_{km}-\omega), \qquad \alpha_{km:mk}=1/\hbar(\omega_{km}+\omega). \quad (3.5)$$

The integrals $I_{ab:cd}$ then lead to the usual pair correlation function

$$\rho_{ab:cd}=\rho_{ac}\rho_{bd}-\rho_{ad}\rho_{bc} \quad (3.6)$$

of a single determinant, and the mean value of the energy (2.4) now includes exchange terms.

To find a more accurate expression for the correlation function and energy we split up the Hamiltonian into $\hat{F}$ and a remainder $\hat{V}$, and measure all energies from the energy of Φ_0. We define $\hat{H}'=\hat{H}-\langle H\rangle$ and $\hat{F}'=\hat{F}-\langle F\rangle$ and then split $\hat{H}'$ into

$$\hat{H}'=\hat{F}'+\hat{V}. \quad (3.7)$$

It can now be shown straightforwardly that

$$\hat{F}'=\eta_k{}^*\eta_k\epsilon_k+(\eta_m{}^*\eta_m-1)\epsilon_m \quad (3.8)$$

and

$$\hat{V}=\tfrac{1}{4}\eta_a{}^*\eta_b{}^*\langle ab \mid cd\rangle\eta_d\eta_c -\eta_a{}^*\eta_b\langle am \mid bm\rangle+\tfrac{1}{2}\langle nm \mid nm\rangle. \quad (3.9)$$

Imagine that $\hat{V}$ is switched on gradually as a perturbation of strength g, with $\hat{H}'(g)=\hat{F}'+g\hat{V}$. At each stage let the exact wave function be $\Psi(g)$

$$\hat{H}'(g)\Psi(g)=E(g)\Psi(g); \quad (3.10)$$

$$E(0)=0, \qquad \Psi(0)=\Phi_0, \qquad A(0)=\alpha \quad (3.11)$$

with energy $E(g)$, polarizability $A(g)$, and density $\rho(g)$. Differentiation with respect to g gives

$$\partial E/\partial g=\langle\Psi(g) \mid \hat{V} \mid \Psi(g)\rangle, \quad (3.12)$$

and we obtain the correlation energy ΔE in terms of the changes $\Delta\rho=\rho(g)-\rho(0)$:

$$\Delta E=\int_0^1\{\tfrac{1}{4}\langle cd \mid ab\rangle\,\Delta\rho_{ab:cd}(g)-\langle am \mid bm\rangle\,\Delta\rho_{ab}(g)\}\,dg. \quad (3.13)$$

This is exact, provided that one can calculate the density changes exactly as a function of g.

Let us now assume that the difference between the exact polarizability $A(g, \omega)$ and the approximate value $\alpha(\omega)$ has been calculated. This difference is called $\Delta A(g, \omega)$, and its integral (2.16) over all frequencies called $\Delta I_{ab:cd}$. We then define the quantities $\Delta\rho'$ and $\Delta E'$ by the relations

$$\Delta\rho'_{ab:cd}=\frac{\hbar}{\pi}\int_0^\infty \Delta A''_{ac:bd}(g, \omega)\,d\omega=\Delta I_{ac:bd} \quad (3.14)$$

$$\Delta E'=\tfrac{1}{4}\int_0^1 \Delta\rho'_{ab:cd}(g)\,\langle cd \mid ab\rangle\,dg. \quad (3.15)$$

Now in (2.17) the two-particle density matrix $\rho_{ab:cd}$ depends on the one-particle one, and so the total change $\Delta\rho_{ab:cd}$ depends on $\Delta\rho_{ab}$ as well as on $\Delta\rho'_{ab:cd}$. So does the total correlation energy ΔE. $\Delta\rho'$ and $\Delta E'$ therefore represent that *part* of the pair-correlation function and correlation energy which depends on the polarizability, and under certain conditions they give the whole effect. Thus in an electron gas the density is uniform and (3.15) is the exact correlation energy.[4]

In this paper we *assume* that $\Delta\rho'$ and $\Delta E'$ represent the approximate correlation function and correlation energy when $\Delta A(g,\omega)$ has been calculated by the time-dependent Hartree–Fock method. Certainly if $\hat{V}$ is regarded as a small perturbation $\Delta\rho_{ab}$ is of order g^2 and its contribution to ΔE is of order g^3, while $\Delta\rho'_{ab:cd}\propto g$ and $\Delta E'\propto g^2$. Thus it *may* be permissible to treat $\Delta E'$ as the main part of the correlation energy.

4. CALCULATION OF THE POLARIZABILITY

A reasonable approximate solution to the time-dependent Schrödinger equation for N electrons would seem to be a single determinant

$$\Phi(t)=\|\psi_1(t)\psi_2(t)\cdots\psi_m(t)\cdots\psi_N(t)\| \qquad (4.1)$$

in which each spin-orbital varies with time according to the Hartree–Fock equations[17]

$$i\hbar(\partial\psi_m/\partial t)=F(t)\psi_m=\sum_a F_{am}(t)\psi_a. \qquad (4.2)$$

The operator $F(t)$ involves the time in two ways. There may be a variable potential $U(t)$ and there are also changes in the Coulomb and exchange fields as the electrons move. This solution would be wrong, because in a stationary state each orbital would have a time factor $\exp(-i\epsilon_m t/\hbar)$ and $\Phi(t)$ itself a factor corresponding to the total energy

$$\epsilon_1+\epsilon_2+\cdots\epsilon_N=\langle F\rangle=\langle H\rangle+\langle G\rangle \qquad (4.3)$$

which includes the electron repulsion energy twice. The difficulty is easily cured by taking the wave function to be

$$\Phi'(t)=\Phi(t)\exp[i\gamma(t)/\hbar], \qquad (4.4)$$

with a phase factor

$$\gamma(t)=\int_0^t\langle G(t)\rangle\,dt, \qquad (4.5)$$

while the orbitals still obey the Eqs. (4.2). For many purposes the phase factor is unimportant and one can use the uncorrected wave function $\Phi(t)$. The proof of these results uses a time-dependent variational principle[18] and is given in Sec. 8.

We now calculate the polarizability $A(\omega)$ directly from the "unperturbed" polarizability $\alpha(\omega)$ of the electrons in the Hartree–Fock ground state Φ_0. The essential point is that the operator $F(t)$ in (4.2) depends on the electron density

$$F_{ab}=U_{ab}+\langle ad\mid bc\rangle\rho_{cd}. \qquad (4.6)$$

Suppose that a small external force $-f(t)$ acts. The density ρ changes linearly so that $F(t)$ differs slightly from its steady value F_0, and the orbitals are solutions of

$$i\hbar(\partial\psi/\partial t)=[F(t)-f(t)]\psi=[F_0-\tilde{f}(t)]\psi. \qquad (4.7)$$

According to (4.7) we can say that the motion of ψ is the same to first order as if F remained fixed at F_0 but a modified *effective external force* $-\tilde{f}(t)$ acted. Thus the change of density under a periodic force is expressed either in terms of $A(\omega)$ and the real force or of $\alpha(\omega)$ and $\tilde{f}$

$$\rho_{ab}(\omega)=\alpha_{ab:cd}(\omega)\tilde{f}_{dc}(\omega)=A_{ab:cd}(\omega)f_{dc}(\omega). \qquad (4.8)$$

[when $\omega=0$ $\rho_{ab}(0)$ must be understood as the difference between ρ_{ab} and its unperturbed average value]. The relation between f and $\tilde{f}$, from (4.6) is

$$\tilde{f}_{qp}(\omega)=f_{qp}(\omega)-\langle qs\mid pr\rangle\rho_{rs}(\omega) \qquad (4.9)$$

and since it must be true whatever the form of f, we obtain a relation between α and A

$$A_{ab:cd}=\alpha_{ab:cd}-\alpha_{ab:pq}\langle qs\mid pr\rangle A_{rs:cd}. \qquad (4.10)$$

In a simplified notation we could write this symbolically as

$$\mathbf{A}=\boldsymbol{\alpha}-\boldsymbol{\alpha}\mathbf{v}\mathbf{A} \qquad (4.11)$$

and find an iterative solution for $\mathbf{A}$ in powers of $\mathbf{v}$

$$\mathbf{A}=\boldsymbol{\alpha}-\boldsymbol{\alpha}\mathbf{v}\boldsymbol{\alpha}+\boldsymbol{\alpha}\mathbf{v}\boldsymbol{\alpha}\mathbf{v}\boldsymbol{\alpha}-\cdots. \qquad (4.12)$$

This is simply the series expansion of the exact relation

$$\mathbf{A}^{-1}=\boldsymbol{\alpha}^{-1}+\mathbf{v}. \qquad (4.13)$$

Here $\mathbf{A}$ and $\boldsymbol{\alpha}$ have to be interpreted as matrices with rows and columns labeled by the pairs of electrons ab, cd. If $\mathbf{v}$ is small (4.12) is a useful expansion; but if it is large one needs to find a direct solution of (4.13), and the easiest way is by considering the time-dependent wave functions $\psi(t)$, as we do in the next section.

$\mathbf{A}(\omega)$ has poles at frequencies where the determinant of $(\boldsymbol{\alpha}^{-1}+\mathbf{v})$ vanishes, that is where "free oscillations" of the density matrix are possible without any external force. They approximate true excitation frequencies of the molecule. Equations (4.12) and (4.13) already give a closed form for A which is used in Sec. 6 to find the correlation energy.

5. FREE AND FORCED OSCILLATIONS

When a small perturbation $-f(t)$ acts on the electrons in their ground state Φ_0 each of the orbitals ψ_m alters slightly and the wave function, to first order in f, becomes $\Phi(t)\exp(-iE_0t/\hbar)$, with

$$\Phi(t)=\Phi_0+\sum_{m,k}C_{mk}(t)\Phi(m\to k), \qquad (5.1)$$

where $\Phi(m\to k)$ is the state in which one electron has jumped from ψ_m into ψ_k. The Hartree–Fock equations of motion (4.2) give

$$\begin{aligned} i\hbar(dC_{mk}/dt)&=(\epsilon_k-\epsilon_m)C_{mk}+\langle kn\mid mj\rangle C_{nj}\\ &\quad+\langle kj\mid mn\rangle C_{nj}^*-f_{km}(t)\\ -i\hbar(dC_{mk}^*/dt)&=(\epsilon_k-\epsilon_m)C_{mk}^*+\langle mn\mid kj\rangle C_{nj}\\ &\quad+\langle mj\mid kn\rangle C_{nj}^*-f_{mk}(t) \end{aligned} \qquad (5.2)$$

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[18] J. Frenkel, *Wave Mechanics, Advanced General Theory* (Clarendon Press, Oxford, England, 1934), p. 435.

for the coefficients,[19] and if the force oscillates with a time factor $e^{-i\omega t}$ the C's contain terms with factors of both $e^{\pm i\omega t}$

$$C_{mk}=X_{mk}\,e^{-i\omega t}+Y_{mk}{}^*\,e^{+i\omega t}$$
$$C_{mk}{}^*=X_{mk}{}^*\,e^{+i\omega t}+Y_{mk}\,e^{-i\omega t} \tag{5.3}$$

owing to the fact that both C and C^* appear in the equation of motion for C. Substitution into (5.2) leads to equations for the X and Y coefficients

$$\begin{aligned}\hbar\omega X_{mk}&=(\epsilon_k-\epsilon_m)X_{mk}+\langle kn\mid mj\rangle X_{nj}\\&\quad+\langle kj\mid mn\rangle Y_{nj}-f_{km}(\omega)\\-\hbar\omega Y_{mk}&=(\epsilon_k-\epsilon_m)Y_{mk}+\langle mn\mid kj\rangle X_{nj}\\&\quad+\langle mj\mid kn\rangle Y_{nj}-f_{mk}(\omega).\end{aligned}\tag{5.4}$$

The solutions of these equations correspond to forced oscillations, but when $f=0$ free oscillations can occur at certain frequencies ω_α. We first study the free oscillations.

It is useful to adopt a double vector notation with bras and kets, so that $|\mathbf{X},\mathbf{Y}\rangle$ stands for the set of coefficients X_{mk}, Y_{mk} and $\langle\mathbf{X},\mathbf{Y}|$ for $X_{mk}{}^*$, $Y_{mk}{}^*$. The equation of motion (5.4) for free oscillations is then written

$$\hbar\omega_\alpha\,|\mathbf{X}^\alpha,-\mathbf{Y}^\alpha\rangle=\mathbf{\Lambda}\,|\mathbf{X}^\alpha,\mathbf{Y}^\alpha\rangle, \tag{5.5}$$

where $\mathbf{\Lambda}$ is a Hermitian matrix made up of 2×2 submatrices. Each pair of excitations mk, nj gives rise to one submatrix

$$\begin{bmatrix}(\epsilon_k-\epsilon_m)\,\delta_{mk:nj}+\langle kn\mid mj\rangle & \langle kj\mid mn\rangle\\ \langle mn\mid kj\rangle & (\epsilon_k-\epsilon_m)\,\delta_{mk:nj}+\langle mj\mid kn\rangle\end{bmatrix} \tag{5.6}$$

and the four elements belong to the components X^*X, Y^*Y, X^*Y, and Y^*X of the vectors.

The ω_α are not eigenvalues of $\mathbf{\Lambda}$ and the vectors $|\mathbf{X}^\alpha,\mathbf{Y}^\alpha\rangle$ are not orthogonal in the usual sense. The oscillations come in pairs at ω_α and $-\omega_\alpha$ with solutions

$$|\mathbf{X}^\alpha,\mathbf{Y}^\alpha\rangle,\,\omega_\alpha\quad\text{and}\quad|\mathbf{Y}^{*\alpha},\mathbf{X}^{*\alpha}\rangle,\,-\omega_\alpha \tag{5.7}$$

and in nuclei zero frequencies may occur.[20] They do not normally occur in molecules unless the Hartree–Fock ground state is degenerate or approaching instability (Sec. 9), and we assume in this paper that all frequencies are nonzero.

The vectors obey an orthogonality relation. To prove it one takes the scalar product of (5.5) with another solution $\langle\mathbf{X}^\beta,\mathbf{Y}^\beta|$

$$\langle\mathbf{X}^\beta,\mathbf{Y}^\beta|\mathbf{\Lambda}\,|\mathbf{X}^\alpha,\mathbf{Y}^\alpha\rangle=\hbar\omega_\alpha\{\langle\mathbf{X}^\beta\mid\mathbf{X}^\alpha\rangle-\langle\mathbf{Y}^\beta\mid\mathbf{Y}^\alpha\rangle\}. \tag{5.8}$$

Now interchange α and β and take the complex conjugate, to show that

$$\hbar(\omega_\alpha-\omega_\beta)\{\langle\mathbf{X}^\beta\mid\mathbf{X}^\alpha\rangle-\langle\mathbf{Y}^\beta\mid\mathbf{Y}^\alpha\rangle\}=0, \tag{5.9}$$

so that the vectors are orthogonal with an indefinite metric. They must also be normalized. Usually $\mathbf{\Lambda}$ is a positive definite Hermitian matrix, and the left-hand side of (5.8) is positive and real when $\alpha=\beta$. This proves that the frequencies are all real and allows us to choose the vectors so that

$$\langle\mathbf{X}^\beta\mid\mathbf{X}^\alpha\rangle-\langle\mathbf{Y}^\beta\mid\mathbf{Y}^\alpha\rangle=\pm\delta_{\alpha\beta} \tag{5.10}$$

for positive and negative ω_α, respectively.

The vectors belonging to $-\omega_\alpha$ are in one sense redundant because of (5.7), but they are needed to make up the complete set of double vectors $|\mathbf{X}^\alpha,\mathbf{Y}^\alpha\rangle$. The completeness relations are unusual too:

$$\sum_{\pm\alpha}|\mathbf{X}^\alpha,\mathbf{Y}^\alpha\rangle\langle\mathbf{X}^\alpha,-\mathbf{Y}^\alpha|=1 \tag{5.11}$$

or

$$\sum_{\alpha>0}|\mathbf{X}^\alpha,\mathbf{Y}^\alpha\rangle\langle\mathbf{X}^\alpha,-\mathbf{Y}^\alpha|-|\mathbf{Y}^{*\alpha},\mathbf{X}^{*\alpha}\rangle\langle\mathbf{Y}^{*\alpha},-\mathbf{X}^{*\alpha}|=1. \tag{5.12}$$

These orthogonality and completeness theorems are altered if there is a zero frequency.[20]

The free oscillation solutions solve the problem of the forced oscillations at any frequency. We define a vector

$$|\mathbf{f},\mathbf{f}^*\rangle=|f_{km}(\omega),f_{mk}(\omega)\rangle \tag{5.13}$$

and write Eq. (5.4) as

$$\hbar\omega\,|\mathbf{X},-\mathbf{Y}\rangle=\mathbf{\Lambda}\,|\mathbf{X},\mathbf{Y}\rangle-|\mathbf{f},\mathbf{f}^*\rangle. \tag{5.14}$$

The solution is expanded in terms of the $|\mathbf{X}^\alpha,\mathbf{Y}^\alpha\rangle$ at both positive and negative frequencies, to give

$$|\mathbf{X},\mathbf{Y}\rangle=\sum_\alpha\pm\frac{|\mathbf{X}^\alpha,\mathbf{Y}^\alpha\rangle\langle\mathbf{X}^\alpha,\mathbf{Y}^\alpha|}{\hbar(\omega_\alpha-\omega)}\,|\mathbf{f},\mathbf{f}^*\rangle. \tag{5.15}$$

Since the Fourier components of the density matrix are

$$\rho_{jn}(\omega)=X_{nj}(\omega),\qquad\rho_{nj}(\omega)=Y_{nj}(\omega) \tag{5.16}$$

or in vector notation

$$|\boldsymbol{\varrho},\boldsymbol{\varrho}^*\rangle=|\mathbf{X},\mathbf{Y}\rangle \tag{5.17}$$

we can deduce the polarizability matrix $A_{ab:cd}(\omega)$. Its only nonvanishing elements are those where each pair ab, cd is of the type mk or km. We rewrite (5.15) as a sum over positive frequencies only, using (5.7) and find that

$$|\boldsymbol{\varrho},\boldsymbol{\varrho}^*\rangle=\frac{1}{\hbar}\sum_{\alpha>0}\left\{\frac{|\mathbf{X}^\alpha,\mathbf{Y}^\alpha\rangle\langle\mathbf{X}^\alpha,\mathbf{Y}^\alpha|}{(\omega_\alpha-\omega)}+\frac{|\mathbf{Y}^{*\alpha},\mathbf{X}^{*\alpha}\rangle\langle\mathbf{Y}^{*\alpha},\mathbf{X}^{*\alpha}|}{(\omega_\alpha+\omega)}\right\}|\mathbf{f},\mathbf{f}^*\rangle. \tag{5.18}$$

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[19] D. J. Thouless, *Quantum Mechanics of Many-Body Systems* (Academic Press Inc., New York, 1961).

[20] D. J. Thouless, Nucl. Phys. **22**, 78 (1961).

The expression in brackets is simply the polarizability A as an operator in bra and ket notation, or rather it is the dispersive part $A'(\omega)$ when ω is not a resonance frequency. The absorptive part $A''(\omega)$ is given by

$$A''(\omega)=(\pi/\hbar)\sum_{\alpha>0}\{|\mathbf{X}^\alpha,\mathbf{Y}^\alpha\rangle\langle\mathbf{X}^\alpha,\mathbf{Y}^\alpha|\,\delta(\omega-\omega_\alpha)$$
$$-|\mathbf{Y}^{*\alpha},\mathbf{X}^{*\alpha}\rangle\langle\mathbf{Y}^{*\alpha},\mathbf{X}^{*\alpha}|\,\delta(\omega+\omega_\alpha)\}. \quad (5.19)$$

The free oscillation solutions thus give complete information about the polarizability, and the integrals $I_{ac:bd}$ are contained in the expression

$$\mathbf{I}=\sum_{\alpha>0}|\mathbf{X}^\alpha,\mathbf{Y}^\alpha\rangle\langle\mathbf{X}^\alpha,\mathbf{Y}^\alpha|. \quad (5.20)$$

For example $I_{jn:mk}$ is the sum of $X_{nj}{}^\alpha X_{mk}{}^{*\alpha}$. A simpler way to interpret these results comes from (2.11). We regard each resonance ω_α as a transition to a fictitious excited state α, to which the transition density is

$$(\rho_{km})_{0\alpha}=X_{mk}{}^\alpha, \qquad (\rho_{mk})_{0\alpha}=Y_{mk}{}^\alpha \quad (5.21)$$

so that any one-electron operator M has the "matrix element"

$$M_{0\alpha}=M_{km}{}^*X_{mk}{}^\alpha+M_{mk}{}^*Y_{mk}{}^\alpha=\langle\mathbf{M},\mathbf{M}^*|\mathbf{X}^\alpha,\mathbf{Y}^\alpha\rangle. \quad (5.22)$$

For example if M is the dipole moment operator $|M_{0\alpha}|^2$ gives the intensity of absorption of radiation at the resonance.

The presence of M_{mk} in (5.22) is expected, since the electron makes a transition from m to k, but the term M_{km} associated with $Y_{mk}{}^\alpha$ represents the reverse process. It reflects the presence of doubly excited electronic configurations in the true *ground* state which are not included in Φ_0. If we had left out the Y terms in (5.4) the results would be exactly equivalent to an ordinary stationary state calculation of $M_{0\alpha}$ in which Φ_0 is the ground state and the excited states Φ_α are "best" linear combinations of the $\Phi(m\rightarrow k)$, chosen to give stationary values to the total energy.

6. CORRELATION ENERGY

The correlation energy of the electron gas in the random-phase approximation[21,22] comes out as the zero-point energy of a set of harmonic oscillators. So does the van der Waals energy of a group of atoms in the time-dependent Hartree theory.[6] A modified theorem holds here.

Let us imagine, as in Sec. 3, that the electron interaction gV is switched on, so that the resonance frequencies $\omega_\alpha(g)$ gradually alter from their initial values ω_{km}. Regarded as a set of harmonic oscillators, their zero-point energy is

$$W(g)=\tfrac{1}{2}\hbar\sum_{\alpha>0}\omega_\alpha(g), \qquad W(0)=\tfrac{1}{2}\hbar\sum_{km}\omega_{km}. \quad (6.1)$$

Our theorem is that the part $\Delta E'$ of the correlation energy (3.15) is

$$\Delta E'=\tfrac{1}{2}[\Delta W-(\partial W/\partial g)_{g=0}] \quad (6.2)$$
$$=\tfrac{1}{4}\sum[\hbar\omega_\alpha-\hbar\omega_{km}-\langle mk|km\rangle]. \quad (6.3)$$

We first require a theorem about the way the oscillations change when the matrix $\mathbf{\Lambda}$ in (5.5) is altered by a small amount $\delta\mathbf{\Lambda}$, so that the vectors and frequencies alter by $|\delta\mathbf{X}^\alpha,\delta\mathbf{Y}^\alpha\rangle$ and $\delta\omega_\alpha$. Extracting the first-order terms

$$\delta\mathbf{\Lambda}|\mathbf{X}^\alpha,\mathbf{Y}^\alpha\rangle+\mathbf{\Lambda}|\delta\mathbf{X}^\alpha,\delta\mathbf{Y}^\alpha\rangle$$
$$=\hbar\,\delta\omega_\alpha|\mathbf{X}^\alpha,-\mathbf{Y}^\alpha\rangle+\hbar\omega_\alpha|\delta\mathbf{X}^\alpha,-\delta\mathbf{Y}^\alpha\rangle \quad (6.4)$$

from (5.5) and expanding $|\delta\mathbf{X}^\alpha,\delta\mathbf{Y}^\alpha\rangle$ in terms of the unperturbed vectors, we find

$$\hbar\delta\omega_\alpha=\pm\langle\mathbf{X}^\alpha,\mathbf{Y}^\alpha|\delta\mathbf{\Lambda}|\mathbf{X}^\alpha,\mathbf{Y}^\alpha\rangle \quad (6.5)$$

and

$$|\delta\mathbf{X}^\alpha,\delta\mathbf{Y}^\alpha\rangle=\sum_\beta\pm\frac{|\mathbf{X}^\beta,\mathbf{Y}^\beta\rangle\langle\mathbf{X}^\beta,\mathbf{Y}^\beta|}{\hbar(\omega^\alpha-\omega_\beta)}\delta\mathbf{\Lambda}|\mathbf{X}^\alpha,\mathbf{Y}^\alpha\rangle. \quad (6.6)$$

The signs are the signs of ω_α in (6.5) and ω_β in (6.6).

The variation of the resonance frequencies comes from this if we substitute $\partial\mathbf{\Lambda}/\partial g$ for $\delta\mathbf{\Lambda}$.

$$\hbar\frac{\partial\omega_\alpha}{\partial g}=[X_{mk}{}^{*\alpha},\ Y_{mk}{}^{*\alpha}]\begin{bmatrix}\langle kn|mj\rangle & \langle kj|mn\rangle\\ \langle mn|kj\rangle & \langle mj|kn\rangle\end{bmatrix}\begin{bmatrix}X_{nj}{}^\alpha\\ Y_{nj}{}^\alpha\end{bmatrix} \quad (6.7)$$

and the sum over all frequencies leads through (5.20) to a sum of the integrals $I_{ac:bd}(g)$

$$\partial W/\partial g=\tfrac{1}{2}\{\langle kn|mj\rangle I_{jn:mk}+\langle kj|mn\rangle I_{jn:km}$$
$$+\langle mn|kj\rangle I_{nj:mk}+\langle mj|kn\rangle I_{nj:km}\}. \quad (6.8)$$

This is to be compared with the exact relation

$$\partial E/\partial g=\tfrac{1}{4}\langle cd|ab\rangle\{I_{ac:bd}(g)-I_{ac:bd}(0)\}, \quad (6.9)$$

which follows from (3.14) and (3.15). Both expressions contain each distinct electron repulsion integral four times. They only differ by a factor of two and the fact that the difference $I(g)-I(0)$ appears in (6.9). Evidently

$$2\frac{\partial E}{\partial g}=\frac{\partial W}{\partial g}-\left(\frac{\partial W}{\partial g}\right)_{g=0}, \quad (6.10)$$

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[21] K. Sawada, K. A. Brueckner, N. Fukuda, and R. Brout, Phys. Rev. **108**, 507 (1957).

[22] D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953).

which is equivalent to (6.2). When $g=0$ the oscillation with frequency ω_{km} has $X_{mk}=1$, $Y_{mk}=0$, and substitution of these modes into (6.7) gives the value of $(\partial W/\partial g)_0$ in (6.3).

In a Hartree calculation *without* exchange one would need to take the correlation energy equal to the whole zero-point energy (6.2) without the factor of one-half. The question whether it is best to neglect exchange and use the whole zero-point energy or to put it in and use half raises some complicated issues. As the electrons are indistinguishable a doubly excited state $(mn\rightarrow kj)$ may be likened to two single-particle oscillations in two ways, either $(m\rightarrow k)$ and $(n\rightarrow j)$ or $(m\rightarrow j)$ and $(n\rightarrow k)$. This appears to be the reason why the correlation energy here is only half the total zero-point energy.

In our previous work on distinguishable systems[6] we found the correlation energy by another method, as an integral[17] of the polarizability at imaginary frequencies, where it has no singularities. Here the analogous integral comes from (3.14)

$$\Delta E'=\frac{\hbar}{4\pi}\int_0^1 dg\int_0^\infty d\xi\langle cd\mid ab\rangle\,\Delta A_{ac:bd}(g,i\xi), \quad (6.11)$$

and gives a useful power series expansion. In the notation of (4.12) the integrand is the trace of a matrix

$$\Delta E'=\frac{\hbar}{4\pi}\int_0^1 dg\int_0^\infty d\xi\,\mathrm{Tr}\,[\Delta\mathbf{A}(g,i\xi)\mathbf{v}] \quad (6.12)$$

$$=-\frac{\hbar}{4\pi}\int_0^\infty d\xi\,\mathrm{Tr}\,[\tfrac{1}{2}(\boldsymbol{\alpha}\mathbf{v})^2-\tfrac{1}{3}(\boldsymbol{\alpha}\mathbf{v})^3+\cdots]$$

$$=\frac{\hbar}{4\pi}\int_0^\infty d\xi\,\mathrm{Tr}\,[\log\,(1+\boldsymbol{\alpha}\mathbf{v})-\boldsymbol{\alpha}\mathbf{v}]. \quad (6.13)$$

Here we have integrated each term of the series (4.12) with respect to g. The integral of the logarithm over imaginary frequencies gives, as before, half the change of zero-point energy,[6] while the part $\boldsymbol{\alpha}\mathbf{v}$ gives the correction $(\partial W/\partial g)_0$.

The first term of the series (6.13) gives exactly the same second-order correlation energy as ordinary second-order stationary state perturbation theory with doubly excited configurations. For the integral

$$-\frac{\hbar}{8\pi}\int_0^\infty d\xi\alpha_{ab:cd}(i\xi)\,\langle df\mid ce\rangle\alpha_{ef:gh}(i\xi)\,\langle hb\mid ga\rangle \quad (6.14)$$

reduces straightforwardly to

$$\Delta E'\simeq-\tfrac{1}{4}\sum_{km}\sum_{jn}\frac{|\langle kj\mid mn\rangle|^2}{\omega_{km}+\omega_{jn}}. \quad (6.15)$$

The first-order correction to the pair-correlation function also agrees with ordinary perturbation theory, but higher terms in both the energy and the correlation function are generally different. We do not discuss the correlation function further in this paper as the results follow from (5.20) in a straightforward way and we plan to examine the details in a later paper on the two-electron problem.

This section completes our main argument, and we now pass on to fill in some of the details.

7. SPIN DEGENERACY

The typical closed shell molecule has all its electrons paired, with two in each space orbital $\phi_m(\mathbf{r})$. The orbitals ϕ_m and ϕ_k are associated with four different electron oscillations, depending on the spin. They correspond to an excitation into either the singlet or triplet excited state formed from the transitions $(m\rightarrow k)$. We use the notation m, m' to label electrons in ϕ_m with α and β spins.

The time-dependent wave function of the oscillating pair of electrons m, m' is the determinant

$$\Phi(t)=\|\,(\phi_m+C_{mk}\phi_k+C_{mk'}\phi_k')$$
$$\times(\phi_m'+C_{m'k}\phi_k+C_{m'k'}\phi_k')\,\|. \quad (7.1)$$

When the coefficients C_{mk} are substituted into (5.4) the oscillations separate out into one singlet with

$$(1/\sqrt{2})\{|X_{mk},Y_{mk}\rangle+|X_{m'k'},Y_{m'k'}\rangle\}=|{}^1x_{mk},{}^1y_{mk}\rangle \quad (7.2)$$

and three degenerate triplet components corresponding to the spin changes $\Delta S_z=1, 0, -1$. Their coefficients are

$$\left.\begin{array}{c}|X_{m'k},Y_{mk'}\rangle\\[4pt](1/\sqrt{2})\{|X_{mk},Y_{mk}\rangle-|X_{m'k'},Y_{m'k'}\rangle\}\\[4pt]|X_{mk'},Y_{m'k}\rangle\end{array}\right\}=|{}^3x_{mk},{}^3y_{mk}\rangle. \quad (7.3)$$

A spin-independent external force $f(t)$ induces only singlet oscillations, but a spin-dependent one triplets. For example, if we split the matrix elements of f into parts

$${}^1f_{mk},{}^3f_{mk}=\tfrac{1}{2}(f_{mk}\pm f_{m'k'}), \quad (7.4)$$

the equations of motion for the singlet coefficients ${}^1x$, ${}^1y$ are

$$\hbar\omega x_{mk}=(\epsilon_k-\epsilon_m)x_{mk}+[2(kn\mid mj)-(kn\mid jm)]x_{nj}$$
$$+[2(kj\mid mn)-(kj\mid nm)]y_{nj}-{}^1f_{km},$$
$$-\hbar\omega y_{mk}=(\epsilon_k-\epsilon_m)y_{mk}+[2(mn\mid kj)-(mn\mid jk)]x_{nj}$$
$$+[2(mj\mid kn)-(mj\mid nk)]y_{nj}-{}^1f_{mk}, \quad (7.5)$$

while the corresponding triplet state ones are

$$\begin{aligned}\hbar\omega x_{mk} &= (\epsilon_k-\epsilon_m)x_{mk}-(kn\mid jm)x_{nj}\\ &\qquad -(kj\mid nm)y_{nj}-{}^3f_{km},\\ -\hbar\omega y_{mk} &= (\epsilon_k-\epsilon_m)y_{mk}-(mn\mid kj)x_{nj}\\ &\qquad -(mj\mid nk)y_{nj}-{}^3f_{mk}.\end{aligned}\tag{7.6}$$

Here, the symbol $(ab\mid cd)$ stands for the ordinary electron repulsion integral $\langle ab\mid G\mid cd\rangle$ over *spinless* orbitals ab, cd and is not antisymmetrized. Electrons of opposite spin move in phase or out of phase with one another in the two types of oscillation.

For example, if M is a function only of the space coordinates of the electron the equivalent matrix elements $M_{0\alpha}$ in (5.22) vanish for all triplets and have the value

$$M_{0\alpha}=\sqrt{2}\langle\mathbf{M},\mathbf{M}^*\mid{}^1\mathbf{x}^\alpha,{}^1\mathbf{y}^\alpha\rangle \tag{7.7}$$

for the singlets. Conversely, if M is an odd function of the spin component S_z it has triplet transition elements

$$\sqrt{2}\langle\mathbf{M},\mathbf{M}^*\mid{}^3\mathbf{x}^\alpha,{}^3\mathbf{y}^\alpha\rangle \tag{7.8}$$

in the oscillation with $\Delta S_z=0$. The polarizability also separates in an obvious way. A spin-independent force ${}^1f(t)$ causes oscillations of the charge density q which are proportional to a space polarizability ${}^1A(\omega)$

$$q_{ab}(\omega)={}^1A_{ab:cd}(\omega)\;{}^1f_{dc}(\omega) \tag{7.9}$$

while the spin polarizability gives the spin density induced by a spin-dependent force. The space polarizability

$${}^1A(\omega)=\frac{2}{\hbar}\sum_{\alpha>0}\left\{\frac{|{}^1\mathbf{x},{}^1\mathbf{y}\rangle\langle{}^1\mathbf{x},{}^1\mathbf{y}|}{\omega_\alpha-\omega}+\frac{|{}^1\mathbf{y}^*,{}^1\mathbf{x}^*\rangle\langle{}^1\mathbf{y}^*,{}^1\mathbf{x}^*|}{\omega_\alpha+\omega}\right\} \tag{7.10}$$

comes from (5.18) and the spin one is completely analogous.

The time-dependent Hartree–Fock theory agrees nicely with the stationary state picture of the excited states in a closed shell molecule and gives the correct spin properties. The frequencies in (7.5) and (7.6) also agree to first order with the stationary-state energy differences. On the other hand, the Hartree–Fock ground state of an open shell usually violates spin and symmetry conservation laws. The time-dependent theory also runs into difficulties in this case. It is important that the time-dependent equations for the small oscillations are linear, unlike the exact Hartree–Fock equations, so that the oscillations have all the symmetry properties of the ground-state Hartree–Fock operator F_0.

8. VARIATIONAL PRINCIPLES

In this section we derive the time-dependent Hartree–Fock equations from a variational principle.[18]

The Schrödinger equation

$$i\hbar(\partial\Psi/\partial t)=H\Psi \tag{8.1}$$

governs the evolution of the wave function from its given value $\Psi(t)$ at time t to its value $\Psi(t)+\tau(\partial\Psi/\partial t)$ at a slightly later time $t+\tau$. In the variational principle we suppose that at all times $\Psi(t)$ has some particular approximate form such as (4.1) and try at each instant to estimate the "best" value of $\partial\Psi/\partial t$ which is consistent with the approximation. Let us suppose that Ψ has been found at a particular instant t, but $\partial\Psi/\partial t$ is unknown. The wave function at time $t+\tau$ close to t then is of the form

$$\Psi(t+\tau)=\Psi(t)-(i/\hbar)\Theta\tau, \tag{8.2}$$

where Θ is an unknown function, independent of τ and arbitrary except for the restriction that $\Psi(t+\tau)$ must have the particular approximate form. Θ is found by minimizing the space integral

$$\int|H\Psi-\Theta|^2\,dv, \tag{8.3}$$

which is equivalent to the condition that the *real part*

$$\mathrm{Re}\int\delta\Theta^*(H\Psi-\Theta)\,dv=0 \tag{8.4}$$

vanishes for all allowed variations of Θ. One cannot conclude from (8.3) that the whole of the integral (8.4) vanishes, as Frenkel postulates, because it is not permissible here to treat $\delta\Theta$ and $\delta\Theta^*$ as independent variables. Although (8.3) is a good variational principle because it leads to a true minimum in every case, it seems that Frenkel's version is incomplete.

If Θ is completely unrestricted (8.3) just gives the Schrödinger equation (8.1). Otherwise it gives an approximate form. Thus if Ψ is formed from linear combinations $C_n(t)\Phi_n$ of fixed functions Φ_n we find that the coefficients derived from (8.4) satisfy

$$i\hbar(dC_n/dt)=H_{nm}C_m \tag{8.5}$$

at each instant of time.

To prove the time-dependent Hartree–Fock equations let us suppose that each orbital has the form

$$\psi_m(t+\tau)=\psi_m(t)-(i/\hbar)\theta_m\tau \tag{8.6}$$

at times close to t. The occupied orbitals ψ_m are not necessarily solutions of the stationary state Hartree–Fock equations, but may be any orthogonal set of functions. It is however still possible to define the operator F, and to complete the orbitals with a set of arbitrary orthogonal "excited" functions ψ_k. The unknown function θ_m is expanded in terms of both occupied and excited orbitals

$$\theta_m=\sum_i a_{im}\psi_i, \tag{8.7}$$

and then the Θ corresponding to the determinant $\Phi(t)$ is a sum of determinants

$$\Theta=\sum_{m}a_{mm}\,\|\psi_1\cdots\psi_m\cdots\psi_N\|+\sum_{km}a_{km}\,\|\psi_1\cdots\psi_k\cdots\psi_N\|$$
$$=[\sum_{m}a_{mm}]\Phi+\sum_{km}a_{km}\Phi(m\rightarrow k), \tag{8.8}$$

including all the singly excited configurations. The matrix elements of the Hamiltonian between these functions are

$$\langle\Phi\mid H\mid\Phi\rangle=\langle H\rangle=\langle F\rangle-\langle G\rangle, \tag{8.9}$$
$$\langle\Phi(m\rightarrow k)\mid H\mid\Phi\rangle=F_{km},$$

and the variation principle gives the coefficients as

$$a_{km}=F_{km},\qquad \sum_{m}a_{mm}=\sum_{m}F_{mm}-\langle G\rangle. \tag{8.10}$$

Since the total wave function $\Phi(t)$ is a product of the ψ_m's only the sum of a_{mm} is relevant, and the coefficients are not completely determined. A satisfactory solution is clearly obtained by calculating the orbitals from the time-dependent Hartree–Fock equations, (4.2) and using the phase factor (4.4).

It is unnecessary to impose orthogonality as a constraint in the variations because F is a Hermitian operator and orthogonality is preserved by the equations of motion. Dirac[7] has shown too that if H is independent of time then the average energy $\langle H\rangle$ is conserved throughout the motion, since it commutes with F. Indeed the mean value of any operator,[23] such as momentum or angular momentum, which commutes with both parts U and G of the Hamiltonian is conserved.

A second variational principle due to Thouless[20] is useful for finding the free oscillations. It states that the resonance frequencies are those at which the quantity

$$|\hbar\omega|=\langle\mathbf{X},\mathbf{Y}\,|\mathbf{A}\,|\,\mathbf{X},\mathbf{Y}\rangle/|\,\langle\mathbf{X},-\mathbf{Y}\,|\,\mathbf{X},\mathbf{Y}\rangle\,| \tag{8.11}$$

is stationary for all variations of the vector $|\,\mathbf{X},\mathbf{Y}\rangle$. One expands $|\,\mathbf{X},\mathbf{Y}\rangle$ as a sum

$$|\,\mathbf{X},\mathbf{Y}\rangle=\sum_{\alpha}C_\alpha\,|\,\mathbf{X}^\alpha,\mathbf{Y}^\alpha\rangle \tag{8.12}$$

and then uses (5.8) to show that

$$|\hbar\omega|=\sum_{\alpha}|\,C_\alpha\,|^2\,|\,\omega_\alpha\,|/[\sum_{\alpha>0}|\,C_\alpha\,|^2-\sum_{\alpha<0}|\,C_\alpha\,|^2]. \tag{8.13}$$

This is stationary for the vectors $|\,\mathbf{X}^\alpha,\mathbf{Y}^\alpha\rangle$, and one may use the variation principle to derive the equations of motion (5.5). It is also possible to set an upper limit to the magnitude of the lowest oscillation frequency, since any trial value of (8.11) must give $|\,\omega\,|\geq|\,\omega_0\,|$.

9. STABILITY CONDITIONS

The Hartree–Fock ground state is only stable if the single determinant $\Phi(t)$ in which ψ_m is altered a little to $(\psi_m+C_{mk}\psi_k)$ always has a higher mean energy than Φ_0. To calculate this energy to second order in C we write $\Phi(t)$ as a sum of determinants

$$\Phi(t)=\Phi_0+C_{mk}\Phi(m\rightarrow k)+\tfrac{1}{2}C_{mk}C_{nj}\Phi(mn\rightarrow kj)+\cdots, \tag{9.1}$$

including both singly and doubly excited configurations, and then the energy shift is

$$C_{nj}{}^*C_{mk}\langle\Phi(n\rightarrow j)\mid H-E_0\mid\Phi(m\rightarrow k)\rangle$$
$$+\tfrac{1}{2}C_{mk}C_{nj}\langle\Phi_0\mid H\mid\Phi(mn\rightarrow kj)\rangle$$
$$+\tfrac{1}{2}C_{mk}{}^*C_{nj}{}^*\langle\Phi(mn\rightarrow kj)\mid H\mid\Phi_0\rangle. \tag{9.2}$$

Substitution of the approximate matrix elements into this expression leads to a quadratic form in the C's and C^*'s which is simply the double scalar product

$$\tfrac{1}{2}\langle\mathbf{C},\mathbf{C}^*\,|\mathbf{A}\,|\,\mathbf{C},\mathbf{C}^*\rangle \tag{9.3}$$

of the vector $|\,\mathbf{C},\mathbf{C}^*\rangle$ with the matrix $\mathbf{A}$. If the ground state is stable the "stability matrix" $\mathbf{A}$ must be positive definite,[12] and all its eigenvalues λ are positive (in some cases a zero value may occur). This is important, because, as we have already seen, the resonance frequencies are all real if $\mathbf{A}$ is positive definite. There must always be *some* single determinant wave function with lowest energy (though it may be degenerate) and it gives a set of real oscillation frequencies (though some may be zero).

10. SUM RULES

An important class of sum rules follow from matrix multiplication and the commutation relations of operators.

$$2\sum_{n}|\,M_{0n}\,|^2\,(E_n-E_0)=\langle\Psi_0\,|\,[M,[H,M]]\,|\,\Psi_0\rangle. \tag{10.1}$$

Here Ψ_0 is the exact ground-state wave function of the system. For example if M is the coordinate q of an electron then

$$[q,[H,q]]=\hbar^2/m, \tag{10.2}$$

and one finds the usual oscillator strength sum rule

$$\sum_{n}f_{0n}=(2m/\hbar^2)\sum_{n}|\,q_{0n}\,|^2\,(E_n-E_0)=1. \tag{10.3}$$

Thouless[20] has shown that these sum rules also hold in the time-dependent Hartree–Fock theory if M is any *one-electron* operator, provided that the excitation energies are taken to be resonances $\hbar\omega_\alpha$ and the fictitious matrix elements $M_{0\alpha}$ from (5.22) are used in the sum. The double commutator is evaluated in Φ_0, the Hartree–Fock ground state.

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[23] D. J. Thouless and J. G. Valatin, Nucl. Phys. **31**, 211 (1962).

We first write the matrix element as

$$M_{0\alpha}=\langle \mathbf{M},\mathbf{M}^* \mid \mathbf{X}^\alpha, \mathbf{Y}^\alpha\rangle=\langle \mathbf{M}, -\mathbf{M}^* \mid \mathbf{X}^\alpha, -\mathbf{Y}^\alpha\rangle, \tag{10.4}$$

so that the left-hand side of (10.1) becomes

$$\begin{aligned}2\sum_{\alpha>0} &\mid M_{0\alpha}\mid^2 \hbar\omega_\alpha\\ &=\sum_\alpha \pm \mid M_{0\alpha}\mid^2 \hbar\omega_\alpha\\ &=\sum_\alpha \pm \langle \mathbf{M}, -\mathbf{M}^* \mid \mathbf{\Lambda} \mid \mathbf{X}^\alpha, \mathbf{Y}^\alpha\rangle\langle \mathbf{X},{}^\alpha -\mathbf{Y}^\alpha \mid \mathbf{M}, -\mathbf{M}^*\rangle\\ &=\langle \mathbf{M}, -\mathbf{M}^* \mid \mathbf{\Lambda} \mid \mathbf{M}, -\mathbf{M}^*\rangle. \end{aligned}\tag{10.5}$$

Here we have used (5.5) and the completeness relations (5.11). The right-hand side breaks up into matrix elements of the Hamiltonian between excited configurations:

$$\begin{aligned}\langle \Phi_0 \mid [M,[H,M]] \mid \Phi_0\rangle &\\ &=\langle \Phi_0 \mid 2MHM-M^2H-HM^2 \mid \Phi_0\rangle\\ &=2M_{nj}M_{mk}^*\langle \Phi(n\rightarrow j) \mid H \mid \Phi(m\rightarrow k)\rangle\\ &\quad -M_{nj}M_{mk}\langle \Phi(nm\rightarrow jk) \mid H \mid \Phi_0\rangle\\ &\quad -M_{nj}^*M_{mk}^*\langle \Phi_0 \mid H \mid \Phi(nm\rightarrow jk)\rangle. \end{aligned}\tag{10.6}$$

The same matrix elements appear in (9.2), and the sum easily reduces to (10.5). If $M=q$ the double commutator is a pure number, and so the oscillator sum rule

$$\sum_{\alpha>0} f_{0\alpha}=(2m/\hbar)\sum_{\alpha>0} \mid q_{0\alpha}\mid^2 \omega_\alpha=1 \tag{10.7}$$

holds exactly in the time-dependent Hartree–Fock theory.

11. FREQUENCIES AS EIGENVALUES

It is useful to transform the equations of motion for the free oscillations so that the vectors $\mid \mathbf{X}^\alpha, \mathbf{Y}^\alpha\rangle$ are the eigenvectors and the frequencies ω_α are the eigenvalues of a Hermitian matrix. This can only be done when the matrix $\mathbf{\Lambda}$ is positive definite (Sec. 9), or has zero eigenvalues, and we use an expansion in the eigenvectors of $\mathbf{\Lambda}$.

These vectors are double vectors of the form $\mid \mathbf{C}_\lambda, \mathbf{C}_\lambda^*\rangle$ and satisfy the equations

$$\mathbf{\Lambda} \mid \mathbf{C}_\lambda, \mathbf{C}_\lambda^*\rangle=\lambda \mid \mathbf{C}_\lambda, \mathbf{C}_\lambda^*\rangle. \tag{11.1}$$

(we use λ both as the eigenvalue and as a label for the vector). They define the variations of the function Φ_0 which make the energy (9.3) stationary. They form a complete orthonormal set, and we normalize them so that

$$\lambda\{\langle \mathbf{C}_\lambda \mid \mathbf{C}_\mu\rangle+\langle \mathbf{C}_\lambda^* \mid \mathbf{C}_\mu^*\rangle\}=\delta_{\lambda\mu}, \qquad \lambda>0. \tag{11.2}$$

We now transform the equations of motion (5.2) by expanding the coefficients $C_{mk}(t)$ as a sum

$$\mid \mathbf{C}, \mathbf{C}^*\rangle=D_\lambda \mid \mathbf{C}_\lambda, \mathbf{C}_\lambda^*\rangle \tag{11.3}$$

where

$$D_\lambda=\lambda\langle \mathbf{C}_\lambda, \mathbf{C}_\lambda^* \mid \mathbf{C}, \mathbf{C}^*\rangle. \tag{11.4}$$

A generalized force is also introduced

$$f_\lambda(t)=\langle \mathbf{C}_\lambda, \mathbf{C}_\lambda^* \mid \mathbf{f}, \mathbf{f}^*\rangle. \tag{11.5}$$

The new equations of motion then become

$$i\hbar(dD_\mu/dt)=(D_\lambda-f_\lambda)G_{\lambda\mu}, \tag{11.6}$$

where $G_{\lambda\mu}$ is a pure imaginary Hermitian matrix

$$G_{\lambda\mu}=\lambda\mu\{\langle \mathbf{C}_\mu \mid \mathbf{C}_\lambda\rangle-\langle \mathbf{C}_\lambda \mid \mathbf{C}_\mu\rangle\}=-G_{\lambda\mu}^* \tag{11.7}$$

and D_μ and f_μ are always real. The free oscillation frequencies ω_α are now the real eigenvalues of G and occur in pairs $+\omega_\alpha$, $-\omega_\alpha$ with the eigenvectors

$$D_\lambda{}^\alpha, +\omega_\alpha \quad \text{and} \quad D_\lambda{}^{*\alpha}, -\omega_\alpha, \tag{11.8}$$

(compare 5.7) which we normalize so that

$$\sum_\lambda D_\lambda{}^{*\alpha} D_\lambda{}^\beta=\delta_{\alpha\beta} \mid \omega_\alpha \mid. \tag{11.9}$$

Under a periodic external force the solution of (11.6) is found by expanding D_λ as a sum of vectors $D_\lambda{}^\alpha$, and its Fourier components are

$$D_{\lambda\omega}=\frac{1}{\hbar}\sum_{\alpha>0}\left\{\frac{D_\lambda{}^\alpha D_\mu{}^{*\alpha}}{\omega_\alpha-\omega}+\frac{D_\lambda{}^{*\alpha} D_\mu{}^\alpha}{\omega_\alpha+\omega}\right\}f_{\mu\omega}=\Pi_{\lambda\mu}(\omega)f_{\mu\omega}. \tag{11.10}$$

Here $\Pi_{\lambda\mu}$ is a generalized polarizability. The $\mid \mathbf{X}, \mathbf{Y}\rangle$ coefficients themselves, according to (11.3) are the Fourier components of $\mid \mathbf{C}, \mathbf{C}^*\rangle$ at frequency ω

$$\mid \mathbf{X}, \mathbf{Y}\rangle= \mid \mathbf{C}_\lambda, \mathbf{C}_\lambda^*\rangle\Pi_{\lambda\mu}(\omega)\langle \mathbf{C}_\mu, \mathbf{C}_\mu^* \mid\cdot\mid \mathbf{f}, \mathbf{f}^*\rangle. \tag{11.11}$$

Comparing this with (5.17) we see that the polarizability $A(\omega)$ has been expressed in terms of the quantities $D_\lambda{}^\alpha$, which are eigenvectors of a Hermitian matrix, and that the vectors

$$\mid \mathbf{X}^\alpha, \mathbf{Y}^\alpha\rangle=D_\lambda{}^\alpha \mid \mathbf{C}_\lambda, \mathbf{C}_\lambda^*\rangle \tag{11.12}$$

evidently represent the free oscillations.

12. REAL AND IMAGINARY FORCES

The Hartree–Fock orbitals of a molecule can always be made real unless the ground state is degenerate; so the stability matrix $\mathbf{\Lambda}$ and the vectors $\mid \mathbf{X}^\alpha, \mathbf{Y}^\alpha\rangle$ are real too. We can classify the eigenvectors of $\mathbf{\Lambda}$ into a real set $\mid \mathbf{C}_\lambda{}^+, \mathbf{C}_\lambda{}^+\rangle$ and a pure imaginary set $\mid \mathbf{C}_\lambda{}^-, -\mathbf{C}_\lambda{}^-\rangle$. These vectors are solutions of

$$\begin{aligned}&(\epsilon_k-\epsilon_m)C_{mk,\lambda}{}^\pm\\ &\quad+[\langle kn \mid mj\rangle\pm\langle kj \mid mn\rangle]C_{nj,\lambda}{}^\pm=\lambda C_{mk,\lambda}{}^\pm.\end{aligned}\tag{12.1}$$

If $\mathbf{A}$ is a $2\nu \times 2\nu$ matrix there are ν vectors of each type. This makes the equations of motion (11.6) very simple because all the $++$ and $--$ elements of the matrix $G_{\lambda\mu}$ vanish, and the equations for the free oscillations take the form

$$\hbar\omega\, D_\mu{}^{+} = D_\lambda{}^{-} G_{\lambda\mu}{}^{-+},$$

$$\hbar\omega\, D_\mu{}^{-} = D_\lambda{}^{+} G_{\lambda\mu}{}^{+-}. \qquad (12.2)$$

Accordingly one can eliminate half the variables and solve for ω^2

$$(\hbar\omega)^2 D_\mu{}^{+} = D_\lambda{}^{+} (G^2)_{\lambda\mu}{}^{++} \qquad (12.3)$$

as the eigenvalues of a matrix with only ν rows. The vectors $D_\lambda{}^{+}$ are real and $D_\lambda{}^{-}$ are imaginary, so that the polarizability $\Pi_{\lambda\mu}$ has real $++$ or $--$ terms, but imaginary cross terms. The plus and minus parts describe the effects of external forces which are even or odd under time reversal, as for example are electric and magnetic fields. This is because the generalized component $f_\lambda{}^{+}$ comes from the real part of the matrix elements f_{mk}, and $f_\lambda{}^{-}$ from the imaginary part. Thus for a real force with $f_\lambda{}^{-}=0$ the equation of motion for $D_\mu{}^{+}$ is

$$(\hbar\omega^2)\, D_\mu{}^{+} = [D_\lambda{}^{+} - f_\lambda{}^{+}] (G^2)_{\lambda\mu}{}^{++}, \qquad (12.4)$$

and looks like a forced harmonic oscillator. The matrix elements

$$(G^2)_{\lambda\mu}{}^{++} = 4\lambda\mu \langle \mathbf{C}_\mu{}^{+} \mid \mathbf{C}_\nu{}^{-} \rangle \nu^2 \langle \mathbf{C}_\nu{}^{-} \mid \mathbf{C}_\lambda{}^{+} \rangle \qquad (12.5)$$

can be reduced a little by using the fact that $\mathbf{C}_\lambda{}^{\pm}$ are solutions of (12.1), and it is quite easy to set up the eigenvalue equation.

13. DIRAC'S DENSITY MATRIX

The whole time-dependent Hartree–Fock approximation can be developed in terms of density matrices without using wave functions at all.[10] This approach depends on the fact that to every time-dependent wave function $\Phi(t)$ which is a single determinant there corresponds a unique Dirac density operator

$$\rho(t) = \sum_{\text{occ}} \mid m(t) \rangle \langle m(t) \mid, \qquad (13.1)$$

which has the properties $\rho^2=\rho$ and $\mathrm{Tr}\,[\rho]=N$. All the information contained in the wave function can also be deduced from the Dirac density. The matrix elements $\langle a \mid \rho \mid b \rangle = \rho_{ab}$ are the same as the components of the one-particle density matrix defined in (2.3), and their equation of motion[7] follows directly from (4.2) and (4.6)

$$i\hbar(d\rho/dt) = [F(t), \rho], \qquad (13.2)$$

or more fully

$$i\hbar(d\rho_{ab}/dt) = [U, \rho]_{ab} + \langle aq \mid rp \rangle \rho_{pq}\rho_{rb} - \langle rq \mid bp \rangle \rho_{ar}\rho_{pq}. \qquad (13.3)$$

This proof depends on the variational principle (8.4) for the wave function, but another approach[9] only uses density operators. The Heisenberg equation of motion of the operator $\hat{\rho}_{ab}$

$$i\hbar(d\hat{\rho}_{ab}/dt) = [\hat{\rho}_{ab}, \hat{H}], \qquad (13.4)$$

and the commutation laws lead to an exact equation of motion in terms of one- and two-particle operators

$$i\hbar(d\hat{\rho}_{ab}/dt) = U_{ar}\hat{\rho}_{rb} - \hat{\rho}_{ar}U_{rb} + \tfrac{1}{2}\langle qa \mid pr \rangle \hat{\rho}_{pr:qb} - \tfrac{1}{2}\hat{\rho}_{ar:pq} \langle pq \mid br \rangle, \qquad (13.5)$$

which also holds for their mean values. The Hartree–Fock approximation consists in the assumption that

$$\rho_{ab:cd} = \rho_{ac}\rho_{bd} - \rho_{ad}\rho_{bc}, \qquad (13.6)$$

and when this is substituted into (13.5) we again find the equations of motion (13.2). The time-dependent Hartree–Fock method thus appears as essentially a density matrix theory.

14. DISCUSSION

We have done the following things in this paper:

(i) Shown how the density fluctuations in the ground state of a molecule, or the polarizability, give information about the one-electron excited states, the pair correlation function, and the energy of the ground state.

(ii) Used the time-dependent Hartree–Fock equations to calculate the polarizability, and describe the formal properties of the free oscillation solutions. The equations can be derived from a variation principle.

(iii) Proved an important part of the correlation energy to be equal to *half* the zero-point energy of the oscillations. When the coupling between electrons is weak the pair correlation function agrees with conventional perturbation theory to first order, and the energy up to second order.

(iv) Described spin degeneracy, sum rules, and other details of the method.

(v) Obtained the main results directly from Dirac's density matrix without using wave functions.

We intend to make detailed quantitative calculations on molecules later and compare the results with other theories.

The methods of this paper have the advantage that they give a simple physical description of correlation effects in both the ground and excited states. They do not have the limitations of perturbation methods or the physical vagueness of some other approximations, and the results agree with perturbation theory in the weak coupling limit. The method also has built-in danger signals because the amplitude of an oscillation often becomes large and unstable when the theory is applied in a wrong way.

The method is a density matrix theory in the sense that it calculates matrix elements rather than wave functions. Indeed one cannot in general construct stationary-state wave functions for a set of electrons which would lead to the same oscillation frequencies and matrix elements as the time-dependent Hartree–Fock theory. This can lead to important inconsistencies[24] in the results. Another limitation is that one treats the electrons as if their polarization by a finite force were perfectly linear, like a harmonic oscillator. In the language of perturbation theory one includes the linear effects to all orders, but leaves out other classes of terms completely. Only a quantitative calculation can decide whether this limitation is important.

The molecular problems for which the methods seem most suited are weak interactions like van der Waals forces, or situations where configurational mixing is an impracticable approach because of the large number of interacting electrons. Examples are the excited states of large conjugated molecules, or excitons in molecular crystals. The theory would be particularly useful for calculating the intensities of the transitions.

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[24] M. A. Ball and A. D. McLachlan, Mol. Phys. (to be published).