Hartree-Fock Equations with a Perturbing Field

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The Hartree-Fock equations under the action of an arbitrary field for any order of perturbation are set up in an integro-differential form. This form appears particularly advantageous for practical computation in such problems as electronic polarizability and electronic structure perturbations caused by nuclear moments. The equations are explicitly written down for a uniform perturbing field and a comparison is made with previous formulations. A wide variety of other applications is also discussed.

I. INTRODUCTION

RECENTLY there has been considerable work on electronic polarization effects in atoms, molecules, and solids. Sternheimer has investigated the perturbation of the atomic core by a nuclear quadrupole[1] and the dipole (uniform field) polarizability of atoms and ions in an external field.[2] Dipole polarizabilities for several other elements have been computed by Sundbom.[3] Das and Bersohn[4] have calculated quadrupole polarizabilities for ions. The author has studied the polarization of an ion in a molecular environment to motivate the choice of molecular wave functions.[5] Callaway[6] has analyzed the contribution of the core polarization to the cohesive energy of alkali metals. In this paper expressions for the perturbed wave functions and energies within the framework of the Hartree-Fock approximation are set up in a general and straightforward manner. The resulting equations are presented in an integro-differential form which is especially suitable for practical computation. In addition to polarizability problems, calculations of the magnetic properties of molecules and the elastic constants of alkali metals find a natural basis in the perturbed Hartree-Fock formalism. A survey of these and similar problems is given.

II. PERTURBED HARTREE-FOCK EQUATIONS[7]

We may assume that the wave functions defined by the perturbed Hartree-Fock problem have been sub-

jected to a unitary transformation such that they form an orthonormal set solving the equation,[8]

$$\mathfrak{IC}_1\psi_i = \mathcal{E}_i\psi_i. \tag{1}$$

ψ_i and $\mathcal{E}_i$ are expanded in powers of the ordering parameter λ:

$$\psi_i = \phi_i + \lambda\phi_i' + \lambda^2\phi_i'' + \cdots, \tag{2a}$$

$$\mathcal{E}_i = \epsilon_i + \lambda\epsilon_i' + \lambda^2\epsilon_i'' + \cdots. \tag{2b}$$

It is then completely straightforward to carry through the problem, but since it must be written out specifically for each type of perturbation, we restrict the problem to a scalar, one-particle perturbing potential in first order, λV. Also, the results are displayed only through first order (i.e., the equations necessary for calculation of a quantity such as the dipole polarizability). In this case the perturbed one-electron Hartree-Fock operator $\mathfrak{IC}_1$, operating on the function $\psi_i(2)$ is:

$$\mathfrak{IC}_1\psi_i(2) = (f_0 + \lambda V)\psi_i(2)$$
$$+ \sum_q \left[\int \psi_q^*(1)\psi_q(1)G\psi_i(2)d\tau_1 \right.$$
$$\left. - \int \psi_q^*(1)\psi_i(1)G\psi_q(2)d\tau_1 \right] = \mathcal{E}_i\psi_i(2),$$

where $G \equiv 2/r_{12}$, and $f_0 =$ one-electron potential and kinetic energy terms. Substituting $\psi_i = \phi_i + \lambda\phi_i' + \lambda^2\phi_i''$ $+\cdots$, and $\psi_q = \phi_q + \lambda\phi_q' + \lambda^2\phi_q'' + \cdots$, the equations for the various orders are obtained by equating equal powers of λ. Thus, the zero-order equation just defines the orthonormal set of unperturbed functions ϕ_i:

$$\mathfrak{IC}_0\phi_i(2) = f_0\phi_i(2) + \sum_q \left[\int \phi_q^*(1)\phi_q(1)G\phi_i(2)d\tau_1 \right.$$
$$\left. - \int \phi_q^*(1)\phi_i(1)G\phi_q(2)d\tau_1 \right] = \epsilon_i\phi_i(2). \tag{3}$$

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The first-order equation determines ϕ_i':

$$(\mathfrak{IC}_0-\epsilon_i)\phi_i'(2)$$
$$= -V\phi_i(2)-\sum_q\left[\int\phi_q{}^{*\prime}(1)\phi_q(1)G\phi_i(2)d\tau_1\right.$$
$$+\int\phi_q{}^*(1)\phi_q{}'(1)G\phi_i(2)d\tau_1$$
$$-\int\phi_q{}^{*\prime}(1)\phi_i(1)G\phi_q(2)d\tau_1$$
$$\left.-\int\phi_q{}^*(1)\phi_i(1)G\phi_q{}'(2)d\tau_1\right]+\epsilon_i{}'\phi_i(2). \quad (4)$$

The higher-order equations can be obtained in the same manner. By multiplying Eq. (4) through $\phi_i{}^*$ and integrating, $\epsilon_i{}'$ is determined. The result is:

$$\epsilon_i{}'=\sum_q\left[\int\phi_q{}^{*\prime}(1)\phi_i{}^*(2)G\phi_q(1)\phi_i(2)d\tau_1 d\tau_2\right.$$
$$+\int\phi_q{}^*(1)\phi_i{}^*(2)G\phi_q{}'(1)\phi_i(2)d\tau_1 d\tau_2$$
$$-\int\phi_q{}^{*\prime}(1)\phi_i{}^*(2)G\phi_i(1)\phi_q(2)d\tau_1 d\tau_2$$
$$\left.-\int\phi_q{}^*(1)\phi_i{}^*(2)G\phi_i(1)\phi_q{}'(2)d\tau_1 d\tau_2\right]$$
$$+\int\phi_i{}^*V\phi_i d\tau. \quad (5)$$

Besides these equations the orthonormality conditions on the ψ_i's are:

$$\int\psi_i{}^*\psi_j d\tau=\delta_{ij}.$$

This leads to:

$$\int\phi_i{}^*\phi_i d\tau=1, \quad \int\phi_i{}^*\phi_j d\tau=0, \quad (6a)$$

$$\int\phi_i{}^*\phi_i{}'d\tau=0, \quad \int\phi_i{}^*\phi_j{}'d\tau=-\int\phi_i{}^{*\prime}\phi_j d\tau, \quad (6b)$$

$$2\int\phi_i{}^*\phi_i{}''d\tau+\int(\phi_i{}')^2 d\tau=0,$$

$$\int\phi_i{}^{*\prime\prime}\phi_j d\tau+\int\phi_i{}^*\phi_j{}''d\tau=-\int\phi_i{}^{*\prime}\phi_j{}'d\tau. \quad (6c)$$

The relations (6a) are the orthonormality conditions on the unperturbed functions while the first relation of (6b) assures that the normalization of ψ_i can be carried out in principle to second order without having and

detailed knowledge of $\phi_i{}''$. All of these relations also can be proved directly from the one-electron equations of various orders. For example, to prove the second relation of (6b) we take the complex conjugate of Eq. (4) multiply by ϕ_j and integrate. If this is added to the first-order equation determining $\phi_j{}'$, multiplied by $\phi_i{}^*$ and integrated, we get the usual type of proof:

$$(\epsilon_i-\epsilon_j)\int\phi_i{}^*\phi_j{}'d\tau=-(\epsilon_i-\epsilon_j)\int\phi_i{}^{*\prime}\phi_j d\tau,$$

which gives (6b).

III. THE ENERGY EXPRESSIONS

The total energy is:

$$E=\int\Psi^*H\Psi d\tau\equiv E_0+\lambda E_1+\lambda^2 E_2+\cdots, \quad (7)$$

where Ψ is the normalized determinantal wave function made up from the functions ψ_i, H is the many-particle Hamiltonian, E_0 is the unperturbed total energy and in the case of a uniform perturbing field E_2 is proportional to the dipole polarizability. The standard expression for the diagonal energy of a single determinant is:

$$\int\Psi^*H\Psi d\tau=\sum_i\int\psi_i{}^*(1)f\psi_i(1)d\tau_1$$
$$+\tfrac{1}{2}\sum_i{}'\sum_j\left[\int\psi_i{}^*(1)\psi_j{}^*(2)G\psi_i(1)\psi_j(2)d\tau_1 d\tau_2\right.$$
$$\left.-\int\psi_i{}^*(1)\psi_j{}^*(2)G\psi_j(1)\psi_i(2)d\tau_1 d\tau_2\right],$$

where $f\equiv f_0+\lambda V$. Equation (2a) is substituted for ψ_i and the terms are ordered according to λ. The one-electron energy terms to second order in λ are then:

$$\sum_i\int\psi_i{}^*(1)f\psi_i(1)d\tau_1=\sum_i\left[\int\phi_i{}^*f_0\phi_i d\tau\right.$$
$$+\lambda\left(\int\phi_i{}^*f_0\phi_i{}'d\tau+\int\phi_i{}^{*\prime}f_0\phi_i d\tau+\int\phi_i{}^*V\phi_i d\tau\right)$$
$$+\lambda^2\left(\int\phi_i{}^*f_0\phi_i{}''d\tau+\int\phi_i{}^{*\prime\prime}f_0\phi_i d\tau+\int\phi_i{}^{*\prime}f_0\phi_i{}'d\tau\right.$$
$$\left.\left.+\int\phi_i{}^*V\phi_i{}'d\tau+\int\phi_i{}^{*\prime}V\phi_i d\tau\right)\right].$$

The two-electron terms are similarly ordered and give a set of Coulomb and exchange integrals. Equating the zero-order terms in Eq. (7), we get the well-known

relation for the unperturbed energy:

$$E_0 = \sum_i \int \phi_i^* f_0 \phi_i d\tau$$

$$+ \tfrac{1}{2} \sum_i{}' \sum_j \left[\int \phi_i^*(1)\phi_j^*(2)G\phi_i(1)\phi_j(2)d\tau_1 d\tau_2 \right.$$

$$\left. - \int \phi_i^*(1)\phi_j^*(2)G\phi_j(1)\phi_i(2)d\tau_1 d\tau_2 \right]$$

$$= \sum_i \epsilon_i - \tfrac{1}{2} \sum_i{}' \sum_j \left[\int \phi_i^*(1)\phi_j^*(2)G\phi_i(1)\phi_j(2)d\tau_1 d\tau_2 \right.$$

$$\left. - \int \phi_i^*(1)\phi_j^*(2)G\phi_j(1)\phi_i(2)d\tau_1 d\tau_2 \right].$$

To simplify the first- and second-order energy expressions we must introduce information from the one-electron equations. Thus to reduce the first-order terms, Eqs. (3) and (6b) are employed:

$$\sum_i \int \phi_i^{*\prime} f_0 \phi_i d\tau$$

$$= \sum_i{}' \sum_j \left[\int \phi_j^*(1)\phi_i^{*\prime}(2)G\phi_j(1)\phi_i(2)d\tau_1 d\tau_2 \right.$$

$$\left. - \int \phi_j^*(1)\phi_i^{*\prime}(2)G\phi_i(1)\phi_j(2)d\tau_1 d\tau_2 \right]. \quad (8)$$

Using the Hermitian property of $\mathcal{3C}_0$, the other one-electron integrals involving f_0 are obtained. By making a change in variable in the double summation, $i \to j$, $j \to i$ and letting $1 \to 2$, $2 \to 1$, it is immediately apparent that all of the two electron integrals cancel, yielding the first-order energy as:

$$E_1 = \sum_i \int \phi_i^* V \phi_i d\tau = \sum_i \int (\phi_i)^2 V d\tau. \quad (9)$$

Relations similar to Eq. (8) can be derived from Eqs. (3) and (4) to reduce the second-order energy terms. The final result is simply

$$E_2 = \text{Real part of } \sum_i \int \phi_i^* V \phi_i' d\tau. \quad (10)$$

The simplicity of E_2 for a one-particle perturbing potential in first order is somewhat misleading. If higher orders of one- and two-particle perturbing potentials are imposed, E_2 will include not only the above but also matrix elements involving the one-particle potential in second order and the two-particle potential in first order and second order.

In our derivation, a specific separation of the one-electron wave functions into spin-dependent and space-dependent parts has been suppressed, and thus we have tacitly assumed the same spacial dependence for α and

β spin. However, the general procedure which has been followed is not restricted to doubly occupied orbitals and may be carried through for any single determinant. Our method of formulation has been built around this idea of a single determinant, each one-electron orbital of which is expanded in a series in powers of λ. An entirely equivalent and sometimes convenient viewpoint is the determinantal expansion of Ψ:

$$\Psi = \Phi_0 + \lambda \sum_{j=1}^N \Phi_j + \lambda^2 \left(\sum_{k=1}^N \Phi_k + \sum_{lm} \Phi_{lm} \right) + \cdots.$$

Φ_0 is the determinant made from unperturbed orbitals. Φ_j and Φ_k are those determinants which have the ith row replaced by ϕ_i' and ϕ_i'', respectively and $\sum_{lm}\Phi_{lm}$ is the sum over all determinants where ϕ_i' has been substituted for the lth row and ϕ_j' for the mth row.

IV. UNIFORM FIELD POLARIZABILITY

Developments in the theoretical description of electronic systems perturbed by external fields has largely been undertaken to predict the uniform field polarizability and the work may be classified into two lines of attack: perturbation methods and variation methods.

A. Perturbation Methods

In this method the wave function for the perturbed system is expanded in a complete set of unperturbed solutions and the expansion coefficients are then determined, e.g., by the familiar second-order perturbation theory formula. Early work was carried out by Vinti[9] and he was able to simplify second-order perturbation theory terms by use of a sum rule. However, from the standpoint of the treatment presented in this article, by far the most interesting paper within the perturbation method frame work is that of Peng.[10] Peng has considered the unperturbed Hartree-Fock equation as an eigenvalue problem for which, in principle, it is possible to obtain a complete orthonormal set of solutions. Expanding ϕ_i', ϕ_i'', etc., in terms of this complete set, he obtains linear algebraic relations analogous to Eq. (4), etc., for his expansion coefficients. He has also written down the expressions for E_0, E_1, and E_2 and these agree with ours. To compute polarizabilities from Peng's formulation, we must determine a large part of the excited eigenfunction spectrum of the unperturbed Hartree-Fock equations. During the period since Peng's paper appeared, the Roothaan procedure[11] has been devised and, for many applications, this has proved to be the most practical computational approach to Hartree-Fock solutions. In the Roothaan procedure, a finite basis set with energy-determined linear coefficients is substituted for the numerical solution of the integro-differential equations, and for simple atoms it is not too difficult to obtain an unperturbed Hartree-Fock

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solution by this procedure. By somewhat similar means, each excited function would be determined separately from already-known functions. However, without the usual qualitative rules available for unperturbed solutions, the choice of basis functions would be much harder and would require considerable experimentation. But the most serious drawback is the slow convergence produced by the inappropriate nature of these excited eigenfunctions. Tillieu and Guy have recently demonstrated this typically slow convergence by calculating the polarizability of the hydrogen atom.[12] The large error still remaining after using eleven terms indicated the probable necessity of including continuum eigenfunctions.

B. Variation Methods

The practical difficulties of convergence and of obtaining many unperturbed excited states that are inherent in the perturbation method has directed almost all of the recent effort toward employing variation methods. This approach centers around representation of the perturbed wave functions as:

$$\Psi = \Psi_0(1+\Phi), \qquad (11)$$

with Ψ_0 the unperturbed function. Hassé[13] and Atanasoff[14] empirically chose wave functions with Φ equal to a constant times the perturbing potential and computed uniform field polarizabilities for one- and two-electron atoms and ions. Molecular polarizability calculations for H_2^+ and H_2 analogous to those of Hassé were worked out by Steensholt[15] and Bell and Long.[16] This choice of Φ can be considered as motivated by Lennard-Jones' approximate treatment of second-order perturbation theory.[17]

Slater and Kirkwood[18] laid the basis for much of the future work by taking

$$\Phi = \sum_{i=1}^{N} V_i R(r_i), \qquad (12)$$

where $V_i =$ the perturbing potential for the ith electron. They formulated the variation problem for a direct determination of the perturbation energy itself. A Hartree product of one-electron functions was assumed for Ψ_0 and the variation procedure then leads to Euler equations in the form of a second-order ordinary differential equation for $R(r)$. For hydrogen they found

$$R(r) = r + (r^2/2).$$

This result is verified by the well-known exact solution of the H atom in a uniform field carried out by Epstein[19] in parabolic coordinates. It also shows that Slater and Kirkwood's form, Eq. (12), is appropriate for low-lying excited states as well. However, a closed-form solution and the separability of the $R(r)$ differential equation depended upon the linearity of V in rectangular coordinates and the spherical symmetry of Ψ_0. In order to develop a workable technique for more general systems, Kirkwood[20] replaced $R(r_i)$ of Eq. (12) by constants, λ_i, and determined these in a straightforward variation calculation. Kirkwood also considered the use of a determinantal wave function for Ψ_0 in place of the Hartree product. A development similar to Kirkwood's was given by Hellmann.[21] Buckingham[22] improved on Kirkwood's work by introducing more flexibility into the perturbed functions. Each one-electron orbital in a determinantal wave function for the system was set up as:

$$\psi_i = \psi_0[1 + V_i R(r_i)], \qquad (13)$$

where $R(r_i) = C_i$ or $C_{i1} + C_{i2}r$, with the C_{ij} as variation parameters. Bravin[23] has followed up the work of Hellmann. He has employed a Hartree product wave function but increased the flexibility of the one-electron orbitals in essentially the same way as Buckingham.

Another scheme for improving Kirkwood's formulation has been developed by Pople and Schofield.[24] For Φ in Eq. (11) they substitute

$$\Phi = \sum_{i=1}^{N} u(r_i),$$

and $u(r)$ is determined by minimization of the perturbation energy. Further, they set $u(r) = Fg(r)\cos\theta$, where $F =$ strength of the electric field. This yields a final ordinary differential equation for $g(r)$ which Pople and Schofield have numerically integrated for Argon (using a Hartree-Fock free-atom wave function for Ψ_0). The relatively small amount of numerical work required in this approach results primarily from the assumption of a single $u(r)$ for all electrons. The shortcomings of Kirkwood's scheme are clearly shown since his method corresponds to $u(r) = Cr$ while the actual form of $u(r)$ turns out to be a monotonic curve not particularly well represented by a straight line.

A somewhat different method of obtaining a suitable variation function has been attempted by Abbott and Bolton for the polarizability of helium.[25] Selected excited states of the free He atom were multiplied by a variation parameter and quite successfully used to describe the distortion produced by the external field.

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The parallel and perpendicular polarizability of H_2 has been calculated with this type of approach by Ishiguro, Arai, Mizushima, and Kotani.[26] The James and Coolidge[27] unperturbed ground state H_2 wave function was employed. Perturbed functions expressed in elliptic coordinates similar to the ground state, but with $\sum_u^+$ and π_g symmetry instead of $\sum_g^+$, were chosen and the energy minimized with respect to linear coefficients. As in the regular perturbation method the difficulty is in obtaining appropriate excited states.

An extensive set of papers has been written by Guy, Harrand, and Tillieu.[28] This work derives from that of Slater and Kirkwood but is developed in a more complete and elegant fashion. A general energy expression is set up and Euler equations are derived that define the distortion of the wave function. A Hartree product of one-electron functions with the form of Eq. (13) is then substituted into the Euler equations. This yields a series of uncoupled one-electron equations in which each perturbed one-electron function depends only upon a single unperturbed orbital and the perturbing field acting on that orbital. Except for a few special cases, these Euler equations do not have a closed form solution and this is related to the situation found by Slater and Kirkwood.

Recently, Sternheimer[2] has reformulated the problem in a manner which leads to a particularly convenient and easy-to-handle differential equation. He adopts a one-particle viewpoint from the beginning and sets up a perturbation theory in the usual way:

$$(H_0 + \lambda V)(\phi_i + \lambda \phi_i') = (\epsilon_i + \lambda \epsilon_i')(\phi_i + \lambda \phi_i').$$

For the uniform field, $(\int \phi_i^* V \phi_i d\tau = 0)$, the first-order equation becomes:

$$(H_0 - \epsilon_i)\phi_i' = -V\phi_i.$$

Sternheimer then introduces information from the unperturbed equation that makes the resulting differential equation especially well suited for direct determination of the perturbed functions. This leads to:

$$(H_0 - \epsilon_i)\phi_i' = [-\nabla^2 + (1/\phi_i)\nabla^2\phi_i]\phi_i' = -V\phi_i. \quad (14)$$

In Eq. (14), as in the work of Guy, Harrand, and Tillieu, each perturbed function is associated uniquely with its unperturbed orbital and, in fact, the two approaches are essentially equivalent. The standard assumption of separability, $u(r,\theta,\varphi) = R(r)Y_l^{|m|}(\theta,\varphi)$, for the one-electron perturbed and unperturbed functions is substituted into Eq. (14) and decomposition of the perturbed function into various angular components is at once apparent. Thus, if ϕ_i is a p function, ϕ_i' will have both an s-like and a d-like part and orthogonality of the angular parts leads to two independent equations. The

division into two equations with separate angular dependence makes each easily reducible to an inhomogeneous differential equation dependent upon r only. They can then be numerically integrated. Numerous dipole polarizabilities have been calculated by Sternheimer[2] and Sundbom[3] using this technique. Wikner and Das[29] also have based their determination of dipole polarizabilities for the helium-like ions on Sternheimer's formulation, but instead of integrating the one-dimensional inhomogeneous equation, they have utilized a trial function similar to Bravin's $(R(r) = C_1 + C_2 r + C_3 r^2$ in Eq. (13)] and evaluated the linear coefficients variationally. The various authors using Eq. (14) have generally employed either Hartree-Fock or Hartree solutions for ϕ_i, depending upon their availability for the particular atom or ion in question.

Equation (14) is to be compared with Eqs. (4) and (5), and we find that three discrepancies are introduced by treating the problem in a one-particle manner. To show these, we first separate the terms of the one-electron operator, f_0:

$$f_0 = -\nabla^2 + (2Z/r).$$

(The one-electron potential energy has been taken as that for an atom with atomic number Z.) Putting this in Eq. (3), we have:

$$(\mathcal{H}_0 - \epsilon_i)\phi_i = 0 = -\nabla^2\phi_i + (2Z/r)\phi_i - \epsilon_i\phi_i + \sum\{\phi_i\},$$

where $\sum\{\phi_i\}$ stands for the summation over the two-electron operators occurring in Eq. (3) and indicates we are operating on ϕ_i. Rearranging the above equation yields:

$$(1/\phi_i)\nabla^2\phi_i = [(2Z/r) - \epsilon_i + (1/\phi_i)\sum\{\phi_i\}]. \quad (15)$$

We now expand the left side of Eq. (4):

$$(\mathcal{H}_0 - \epsilon_i)\phi_i' = -\nabla^2\phi_i' + \phi_i'[(2Z/r) - \epsilon_i + (1/\phi_i')\sum\{\phi_i'\}].$$

The left side of Sternheimer's equation [Eq. (14)] is obtained by substituting Eq. (15) for the bracket above resulting in:

$$(\mathcal{H}_0 - \epsilon_i)\phi_i' = -\nabla^2\phi_i' + \phi_i'[(1/\phi_i)\nabla^2\phi_i]$$
$$= \{-\nabla^2 + [(1/\phi_i)\nabla^2\phi_i]\}\phi_i'.$$

The approximation is that

$$\sum\{\phi_i'\} = (\phi_i'/\phi_i)\sum\{\phi_i\}.$$

Writing each side of this out gives:

$$\sum\{\phi_i'\} = \sum_q \left\{ \int \phi_q^*(1)\phi_q(1)G\phi_i'(2)d\tau_1 - \int \phi_q^*(1)[\phi_i'(1)]G\phi_q(2)d\tau_1 \right\},$$

$$(\phi_i'/\phi_i)\sum\{\phi_i\} = \sum_q \left\{ \int \phi_q^*(1)\phi_q(1)G\phi_i'(2)d\tau_1 - \int \phi_q^*(1)\left[\phi_i(1)\frac{\phi_i'(2)}{\phi_i(2)}\right]G\phi_q(2)d\tau_1 \right\}.$$

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The difference in the operators occurs only in the exchange terms and thus, if we had initially adopted the Hartree rather than Hartree-Fock method in Sec. II, the one-electron approach would have yielded the correct result for the left side of the equation defining the first-order perturbed function. This is partly responsible for the close similarity of Sternheimer's method to that of Guy, Harrand, and Tillieu. We know also that for an atom or simple molecule the Hartree-Fock solution is rather well approximated by a Hartree solution and so for such cases the left side approximation in the first-order perturbed equation may not be a severe one.

The second discrepancy can be seen by writing out all of the two-electron terms in Eq. (4) and considering only the diagonal components, $i=q$. The six two-electron integral operators cancel out in pairs and this part of ϵ_i' is also zero for a uniform field or any perturbing potential odd under a coordinate inversion. Equation (4) is reduced to

$$(f_0 - \epsilon_i)\phi_q'(2) = -V\phi_q(2),$$

and this is just the $i=q$ term of Eq. (14). It is thus off-diagonal Coulomb and exchange operators which are omitted from the right side of Sternheimer's equation and similarly from the equations of Guy, Harrand, and Tillieu. These terms mix in the other perturbed and unperturbed functions and act as a screening potential.

The third omission is the Coulomb and exchange integrals in ϵ_i' which do not arise in a one-particle approach. It may be further noted that neither Guy, Harrand, and Tillieu's method nor Sternheimer's is exactly equivalent to a Hartree formulation because if we omit all of the exchange terms in Eq. (4) the Coulomb operators still mix ϕ_q and ϕ_q' into the equation for ϕ_i' and prevent an uncoupling.

In spite of these discrepancies, all of the relations (6) can be proved directly from Eq. (14), as well as Eq. (4). In addition, Sternheimer obtains the same expressions for E_1 and E_2 as we have given, although they are not derivable from a many-particle standpoint. Another similarity between Eq. (4) and Eq. (14) concerns the symmetry of the perturbed solutions. We noted above that for Sternheimer's equation an unperturbed p function gives rise to s- and d-like perturbed solutions. The general symmetry relation between the perturbed and unperturbed functions is obvious from Eq. (14). Thus for a perturbing potential which is odd under inversion like the uniform field: even ϕ_i's lead to odd ϕ_i's and visa versa. For Eq. (4), the symmetry relations are not so obvious but nevertheless are the same as for Eq. (14). ϕ_i' may be written as a sum of odd and even parts and, if V is odd, we find Eq. (4) splits into two equations, one containing the perturbing potential and the other not. The relation which lacks V is an eigenvalue equation which in general has no solution other than the null one for ϕ_i'. ϵ_i' does not appear in the equation which includes V, again in agreement with Eq. (14).

At the end of part A in this section, we discussed the

computational difficulties to be expected with the perturbation approach. Solution of the integro-differential equations resulting from our method, even though convergence difficulties are avoided, may also appear formidable. Fortunately such is not the case. Our formulation of the perturbed Hartree-Fock equations should be viewed as an extension of Sternheimer's work and for practical computation the only logical procedure is to use solutions of his one-particle equations for the initial trial functions. As in the standard unperturbed Hartree-Fock problem, an iterative technique leading to a self-consistent solution is necessary, but numerical integration of the perturbed radial equation, as well as the quadratures required for the Coulomb and exchange terms, can be computed by any of a number of schemes that now generally exist as subroutines for high-speed digital computers. In fact, computer programs for the automatic computation of free-atom Hartree-Fock solutions have already been constructed by several groups and the perturbed equations should not be appreciably more difficult to handle.

C. Statistical Methods

For completeness, a few comments on statistical methods are appropriate. Gombás[30] has developed a statistical theory for application to the uniform perturbing field problem that incorporates the Fermi-Amaldis correction and introduces an energy determined variable parameter in the electron charge density. On this model the theoretical polarizability is always greater than the experimental value. Gombás reports sizable errors for light atoms and ions but satisfactory results for heavy ones. Sternheimer[31,2] has investigated the feasibility of employing the Thomas-Fermi scheme to evaluate the field at the nucleus induced by an external field acting on an atom or ion. He finds that the incorrect behavior at large r makes this model inadequate. For the same reason, it also should be unsatisfactory for the prediction of dipole polarizabilities. In the Thomas-Fermi-Dirac case, Sternheimer has shown that, while some improvement over Thomas-Fermi results is achieved, the induced field is far too large for low Z atoms and ions.

V. OTHER APPLICATIONS OF THE THEORY

Perturbation theories closely related to the Hartree-Fock approach have been applied to a wide range of atomic, molecular, and solid-state problems in addition to the uniform field polarizability discussed above. In these cases the perturbed Hartree-Fock equations can help to unify work in different areas that is similar but has been carried out independently in each area.

The perturbing field that gives rise to a distortion in the electronic structure can be, of course, an internal field such as the electric quadrupole of a nucleus, as

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well as the uniform external field discussed above. This is the basis of Sternheimer's work on antishielding corrections in the interpretation of nuclear quadrupole moment measurements.[1] He has also calculated magnetic hyperfine-structure corrections to the magnetic field at the nucleus due to the current induced in the electronic core by an external valence electron.[32] Schwartz[33] has considered Sternheimer's hyperfine-structure corrections in the framework of the allowed excitations of the unperturbed Hartree-Fock equations. His objections are closely related to ours and represent the sort of comparison to be made between Sternheimer's approach and the perturbation theory treatment carried out by Peng[10] (see part A of IV).

The quadrupole polarizability, α_q, comes from an external perturbing potential of the form:

$$V_q = \mathfrak{F}r^2(3\cos^2\theta - 1),$$

and is defined as the induced quadrupole moment divided by the field gradient. Values of α_q for a number of atoms and ions have been computed by Sternheimer,[2] and by Das and Bersohn.[4] The latter follows Sternheimer's theory but substitutes a simple variation function for the numerical integration. (See note on Wikner and Das. These latter authors also have used this procedure to compute nuclear quadrupole moment antishielding corrections for heavy ions.[34])

A natural application of perturbation theory for external electric fields is the Van der Waals force between two atoms. The perturbing potential for the dipole-dipole Van der Waals term is:

$$V_{DD} = \frac{2}{R^3}\sum_{i=1}^{N_1}\sum_{j=1}^{N_2}(x_ix_j' + y_iy_j' - 2z_iz_j'),$$

where R = internuclear distance. The prime and unprimed coordinate systems represent the coordinates of the electrons in each separate atom, N_1 is the number of electrons in atom 1, N_2 is the number comprising 2, and the z axis is taken to be that connecting the centers. The evolution of the Van der Waals problem has proceeded along the same lines as the uniform field polarizability. Slater and Kirkwood,[17] Buckingham,[35] and Pople and Schofield[24] each applied their uniform field polarizability techniques to the dipole-dipole term. In fact, it is well known that these methods lead to a Van der Waals energy term that is proportional to the product of the uniform field polarizability of the two isolated atoms. Their methods start from Eq. (11) with

$$\Psi_0 = \Psi_{01}\Psi_{02},$$

$$\Phi = V_{DD}R(r_i, r_j').$$

For many electron atoms, $R(r_i, r_j')$ has been taken as a

product of r_i-dependent and r_j'-dependent factors, and the theory proceeds in the same manner as the uniform field problem. Buckingham also considered the dipole-quadrupole term for two like atoms and found that the ratio of the dipole-dipole to dipole-quadrupole coefficients in the energy expansion could be simply related to the atomic diamagnetic susceptibility.

There are several problems in spectroscopy and in electron scattering where the primary interest is in an accurate description of a single outer electron or a single outer shell. The unperturbed Hartree-Fock wave function for such an electron takes into account the average effect of this electron on the other but not the effect of its instantaneous field on the atomic core. Various attempts have been made to include this polarization term in the effective potential for an outer electron.[36] At large r, the behavior is $\frac{1}{2}(\alpha/r^4)$, where α is the dipole polarizability. Bates[37] has considered this and a related form to interpret photo-ionization of atomic potassium, and he found the excitation cross section very sensitive to the polarization correction. To obtain the correct form for all r, a treatment similar to Sternheimer's or that we have given is required, and it appears likely that this could lead to ionization energies that agree more accurately with the observed optical spectra terms and perhaps even to wave functions able to predict satisfactory transition probabilities. Polarization effects in the scattering of slow electrons by atomic oxygen has been considered in some detail recently by Temkin.[38] In his numerical work, he used only a dipole distortion (uniform field) and only the dominant perturbed orbital computed by Sternheimer's approximation, but even this led to a significant improvement in results.

In the theory of molecular structure, there are several classic problems whose solutions in principle are based on the perturbed Hartree-Fock equations. One of the most important of these is the study of inductive and electrometric perturbations in conjugated molecules. All of the treatments are based on the perturbation method (Part A, Sec. IV). Coulson and Longuet-Higgins[39] devised an independent electron model where the two-electron terms are omitted. Pople[40] used the exact Hamiltonian and set up the equations in the framework of the Roothaan scheme but assumed matrix elements between configurations made from substitution of a single excited orbital to be zero. Lefebvre and Moser[41] have given the complete equation and these are thus identical to those of Peng.[10] For all

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[40] J. A. Pople, Proc. Roy. Soc. (London) **A233**, 233 (1955); J. A. Pople and P. Schofield, Proc. Roy. Soc. (London) **A233**, 241 (1948).
[41] R. Lefebvre and C. Moser, *Calcul des fonctions d'onde moléculaire*, (Centre national de la recherche scientific, Paris, 1958), p. 109.

of this work, calculations have been carried out in a very approximate and semi-empirical way, but the results have been of great value to the understanding of chemical phenomena. The various approximations are concerned with the details of the specific problem, and our purpose here is only to make connection with the general formalism.

Another molecular application has been made by Allen.[5] He solved Sternheimer's equations for a point charge field acting on a fluorine ion in an effort to ascertain what type of distorted basis functions should be employed to describe the hydrogen fluoride molecule.

Tillieu and Guy[42] have given theory and examples for the determination of the magnetic susceptibility of molecules with no permanent moment. The perturbing term in the Hamiltonian is:

$$V_\chi = -\beta \mathbf{H} \cdot \mathbf{M},$$

where $\mathbf{H}$ is the applied magnetic field, and $\mathbf{M}$ is the orbital moment operator. The perturbed wave function is assumed to be a Hartree product of functions:

$$\psi_i = \psi_0(1 + \mathbf{H} \cdot \mathbf{g}),$$

where $\mathbf{g}$ is a vector function of the electron coordinates. Minimization of the energy with these functions yields the equations satisfied by $\mathbf{g}$ and the high-frequency terms in the paramagnetic susceptibility[43] may then be computed. Calculations of the diamagnetic susceptibility and magnetic shielding for molecules have been made by Das and Bersohn and Ghose.[44] Their work is based on the Sternheimer formulation but is carried through by the choice of easily manageable variation functions for the perturbed solutions. The techniques adopted by Tillieu et al. and Das et al. for these magnetic properties follow the same lines that we have discussed and compared for the uniform field problem.

In solid state applications, as in molecular structure, a number of major problems utilize the perturbed Hartree-Fock formalism as the central tool in carrying out the solution. Bardeen's early work on the conductivity of alkali metals[45] is essentially equivalent to a first-order perturbation method treatment in the Hartree approximation. The difference between the rigid ion potentials at their equilibrium and displaced positions is the perturbing potential. The resulting change in the self-consistent field of the valence electrons produced by distortion of the crystal was then calculated with plane wave eigenfunctions.

Fuchs and Peng[46] applied Peng's perturbed Hartree-Fock formalism[10] to the calculation of the elastic constants in alkali metals. The perturbation was limited to a homogeneous lattice deformation with the assumption of a spherical atomic cell and a spherical distribution of ions outside the cell. Wigner-Seitz solutions were used for the unperturbed functions. The difficulties inherent in the determination of the excited eigenfunction spectrum of the unperturbed equations were avoided by neglecting the terms dependent upon the first-order perturbed functions. Physical arguments and the properties of the Wigner-Seitz solutions justify the approximations for this application and their results agree well with experiment.

Undoubtedly the most penetrating analysis and comprehensive use of Peng's equations[10] for solid state problems is Herring's paper on the energy band description of the Bloch wall energy.[47] Herring assumes a small sinusoidally varying perturbation torque in first order which tends to rotate the magnetization vector about an axis perpendicular to the direction of magnetization and with the perturbation theory he derives several general results of spin wave theory. Because the problem is that of a metal, one must be concerned with partially-filled bands and the possibility of lowering the energy through a choice of occupation numbers different from those of the unperturbed state. This latter question could be important for electromeric perturbations in special classes of molecules as well as metals, but it does not arise in the other applications we have considered. In an appendix to his paper, Herring proves that for a first-order perturbing potential which is odd under inversion lowering of the energy by such a reshuffling will only occur in a higher order than λ^2. This follows directly from the fact that there is no first-order change in the one-electron energy parameter with an odd perturbing potential. Herring's discussion of this case is similar to that we have given for the uniform field in part B of Sec. IV.

Finally, Callaway[6] has estimated the contribution of the core polarizabilities to the cohesive energy of lithium, sodium, and potassium. His perturbing potential is the electrostatic potential between a core electron (1) and a valence electron (v), $2/r_{1v}$. He makes a multipole expansion of this potential and keeps only the dipole term. Sternheimer's equation is used, but the region $r_1 > r_v$ is neglected, i.e., the core electron is assumed to spend a negligible time outside the valence electron. An especially valuable point in Callaway's paper is his estimate of the Coulomb and exchange integrals neglected in Sternheimer's formulation. For his problem and using lithium as a test case, he finds only a small change except near the origin.

VI. ACKNOWLEDGMENT

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an article by Kaneko on the uniform field polarizability of rare gas atoms has appeared.[48] Kaneko has carried out a numerical calculation on helium using both the exact first order perturbed Hartree-Fock equation and Sternheimer's equation. He finds that Sternheimer's approximation gives a value 12.5% too large.

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Elastic Scattering of Alpha Particles by O16†

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Absolute cross sections for the elastic scattering of alpha particles by O16 have been measured in a differentially pumped gas scattering chamber. The measurements were made for laboratory energies from 3.7 to 6.5 Mev, corresponding to 7.7- to 9.9-Mev excitation in Ne20, at center-of-mass angles of 168.9°, 149.4°, 140.8°, 125.3°, and 90.0°.

Narrow resonances were observed at bombarding energies of 5.002, 5.11, 5.190, 5.432, 5.532, and 6.030 Mev. The data were analyzed in terms of Wigner-Eisenbud dispersion theory to find the spins, parities, resonant energies, widths, reduced widths, and characteristic energies of the levels. The resonances observed correspond to states in Ne20 with the following excitation energies, spins, and parities: 8.755(1−), 8.84(5−), 8.905(1−), 9.099(4+), 9.179(3−), and 9.577 Mev (2+). In order to obtain a good fit to the data, it was necessary to assume the existence of two broad overlapping resonances, one at ~8.7-Mev excitation (0+) and the other at ~8.8 Mev (2+). There is also some evidence for the presence of a broad 4+ level at an energy higher than 9.9-Mev excitation in Ne20.

I. INTRODUCTION

THEORETICAL developments in the last few years have aroused interest in the nuclei with atomic number just above that of the doubly closed shell nucleus O16. Shell model calculations for nuclei of masses 17, 18, and 19[1] and collective model calculations for nuclei of masses 19[2,3] and 25[4] have been performed. Both types of calculations have been very successful in predicting the spins and parities of the lower excited states.

An experimental determination of the spins and parities of the states of Ne20 would be of the greatest importance in further testing the theoretical predictions of the proposed models. The elastic scattering of alpha particles by O16 provides an effective method for the investigation of the $T=0$ levels of Ne20 above 5-Mev excitation. Since the spins of both particles are zero, the only possible combinations of total angular momentum

and parity for the levels which can be seen are even J-even parity and odd J-odd parity. Elastic scattering and capture are the only energetically possible processes in the energy region covered. The (α,γ) process is negligible compared with the probability of particle emission. For the case of spin zero on spin zero scattering with no reactions present, the partial wave analysis of excitation curves taken at several angles and the subsequent interpretation according to dispersion theory are, in principle, relatively simple.

The elastic scattering of alpha particles by O16 from 0.94- to 4.0-Mev bombarding energy has previously been investigated by Cameron.[5] Five levels in Ne20 were found in the region of excitation from 5.5 to 7.9 Mev. The present experiment extends the energy range studied from 4.0- to 6.5-Mev bombarding energy. This same energy range had been studied much earlier by Ferguson and Walker,[6] who used RaC′ as an alpha-particle source. They found two resonances, one at 5.5-Mev and the other at 6.5-Mev bombarding energy. A probable assignment of 1− was made for both of them.

II. EXPERIMENTAL APPARATUS

The scattering chamber and associated equipment used for the measurement of the absolute cross sections

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