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Molecular hyperpolarizabilities. I. Theoretical calculations including correlation

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Static polarizabilities and hyperpolarizabilities for molecules are investigated at the correlated level. The finite-field, coupled Hartree-Fock theory is used as a zeroth-order approximation, with correlation included by using the linked-diagram expansion and many-body perturbation theory, that includes single, double, and quadruple excitation diagrams. The theory is illustrated by studying the hydrogen fluoride molecule. It is demonstrated that the correlation effect for the hyperpolarizabilities $\overleftrightarrow{\beta}$ and $\overleftrightarrow{\gamma}$ can be quite large. The average polarizability and dipole moment of HF are in excellent agreement with experiment. The relative importance of the various types of diagrams contributing to electric field properties are discussed. The dependence of the computed hyperpolarizability on basis sets is also investigated.

I. INTRODUCTION

The nonlinear optical properties of gases have been of experimental interest for several years.[1-7] Recently, a number of real and potential laser applications utilizing the frequency-tripling properties of metal vapors and other atomic gases have been suggested.[8-10] Similar devices employing polar molecules oriented in an electric field can be envisioned for frequency-doubling applications. The utility of such novel devices will be ultimately determined by properties of the atomic and molecular higher polarizability tensors, but little information on these quantities currently exists.

Hyperpolarizabilities may be deduced experimentally from direct observations of harmonic generation in gases[3-5] and from measurements of the Kerr effect.[6,7] However, the experiments are difficult and the range of uncertainty is often large. Since hyperpolarizability is a property of a single atom or molecule, it may also be predicted from quantum-mechanical calculations. Hence it is important to have reliable theoretical predictions for higher polarizabilities to complement the experimental efforts.

While some coupled Hartree-Fock (CHF)[11] level calculations of atomic hyperpolarizabilities are available, mostly for inert gases,[12] very few *ab initio* calculations of molecular hyperpolarizabilities have been attempted,[13-16] and none of these has yet shown any kind of agreement with experiment.[4] The molecular calculations which have been made frequently employ inadequate basis sets or are carried out at the level of uncoupled Hartree-Fock perturbation theory.[13,17] Only a few previous studies have even used the full CHF method,[14-16] with no work, at all, on molecular hyperpolarizabilities at the correlated level. Recent papers have addressed the question of picking adequate basis sets for polarizabilities,[18-20] but the accurate inclusion of correlation effects is still expected to be a necessity if a reliable predictive theory of hyperpolarizabilities is to be developed. Some recent communications have demonstrated the importance of correlation for the dipole polarizability,[18,20-22] and one would anticipate an equally large, or even larger, correlation effect for the hyperpolarizabilities.

Recent developments in many-body perturbation theory (MBPT)[23-27] and the coupled-cluster approaches (CCA),[25,28,29] have made it possible to include correlation in a sufficiently tractable manner to include a very large part of the net correlation effect in molecular calculations[25,30] even though comparatively large basis sets are required in hyperpolarizability determinations.

In the following, we report a study of the hyperpolarizabilities of the HF molecule, considering correlation effects due to single, double, and quadruple excitations.[25] HF provides a convenient example for this initial study since a numerical CHF result has been obtained for the parallel components of the second- and third-order polarizability by Christiansen and McCullough,[16,19] and this result may be used to eliminate some uncertainty in chosing a reliable basis set.

II. HIGHER DIPOLE POLARIZABILITIES

The energy of a molecule in an external field $\mathcal{E}$ may be written in a power series as

$$W(\vec{\mathcal{E}}) = W(0) - \mu_i\mathcal{E}_i - (2!)^{-1}\alpha_{ij}\mathcal{E}_i\mathcal{E}_j - (3!)^{-1}\beta_{ijk}\mathcal{E}_i\mathcal{E}_j\mathcal{E}_k - (4!)^{-1} \times \gamma_{ijkl}\mathcal{E}_i\mathcal{E}_j\mathcal{E}_k\mathcal{E}_l \cdots , \quad (1)$$

where the summation over repeated indices is assumed. $\mathcal{E}_i$ is a component of the external field, μ_i is a component of the permanent dipole, α_{ij} a polarizability, and β_{ijk} and γ_{ijkl} are, respectively, the second and third polarizabilities.[1-4] A component of the total dipole moment, p_i, is obtained from the derivative $\partial W/\partial\mathcal{E}_i$, which is composed of the permanent moment and an induced moment due to the higher-order terms,

$$-\left(\frac{\partial W}{\partial\mathcal{E}_i}\right) = -p_i = \mu_i + \alpha_{ij}\mathcal{E}_j + (2!)^{-1}\beta_{ijk}\mathcal{E}_j\mathcal{E}_k + (3!)^{-1}\gamma_{ijkl}\mathcal{E}_j\mathcal{E}_k\mathcal{E}_l\cdots . \tag{2}$$

The production of second and third harmonic generation follows from the fact that the $\overleftrightarrow{\beta}$ and $\overleftrightarrow{\gamma}$ in term in Eq. (2) involve products of electric field components. Hence for $\mathcal{E}_i = \mathcal{E}_{0i}\sin\omega t$, we have

$$\mathcal{E}_i^2 = \mathcal{E}_{i0}^2\sin^2\omega t = \tfrac{1}{2}\mathcal{E}_{i0}^2(1-\cos 2\omega t),$$

and the $\cos 2\omega t$ term gives rise to frequency doubling.[1] Similarly, the third power in $\mathcal{E}$ is responsible for frequency tripling.[1]

The polarizabilities $\overleftrightarrow{\alpha}$, $\overleftrightarrow{\beta}$, $\overleftrightarrow{\gamma}$ are said to be second-, third-, and fourth-order properties, respectively, based on the order of the external field in the energy expansion of Eq. (1), while the permanent dipole moment is first order. It may be shown that a Hartree-Fock wave function will predict a first-order property, like the permanent dipole moment, to a comparatively good accuracy because the first correlation corrections vanish,[31,32] but there is no similar reason to expect the CHF theory[11,33] to be adequate for the higher-order properties.[18,21,22] Furthermore, for even highly accurate first-order properties and especially higher-order properties, correlation must be considered.

III. MANY-BODY PERTURBATION THEORY

The coefficients in Eq. (1) can be obtained directly from perturbation theory or by using finite-field methods. Choosing the latter, temporarily, we may write the Hamiltonian for the perturbed molecule as

$$\mathcal{H}(\vec{\mathcal{E}}) = \mathcal{H} + \lambda\Omega(\vec{\mathcal{E}}) = F_0 + V + \lambda\Omega(\vec{\mathcal{E}}) \tag{3}$$

and

$$F(\vec{\mathcal{E}}) = F_0 + \lambda\Omega(\vec{\mathcal{E}}), \tag{4}$$

$$\lambda\Omega(\vec{\mathcal{E}}) = \lambda\sum_{i=1}^{N}\omega(i) = -\sum_{i=1}^{N}\vec{\mathcal{E}}\cdot r(i), \tag{5}$$

$$V(\vec{\mathcal{E}}) = \sum_{i<j} r_{ij}^{-1} - \sum_i u(i,\vec{\mathcal{E}}). \tag{6}$$

F_0 is the usual independent particle self-consistent-field (SCF) effective Hamiltonian; hence

$$F(\vec{\mathcal{E}}) = \sum_i [h(i) + u(i,\vec{\mathcal{E}}) - \vec{\mathcal{E}}\cdot\vec{\mathrm{r}}(i)] \tag{7}$$

$$u(1,\vec{\mathcal{E}}) = \sum_j \int \chi_j^*(\vec{\mathcal{E}};2) r_{12}^{-1}\chi_j(\vec{\mathcal{E}};2)\,d\tau_2, \tag{8}$$

and in the general case the molecular orbitals $\{\chi_j\}$ are field dependent.

If we are only interested in the SCF solution in the presence of the field, then V in Eq. (3) may be neglected. This defines the CHF model, with the field-dependent solutions

$$\underline{F}(\vec{\mathcal{E}})\underline{C}_p(\vec{\mathcal{E}}) = \underline{\Delta}\,\underline{C}_p(\vec{\mathcal{E}})\underline{\epsilon}_p(\vec{\mathcal{E}}). \tag{9}$$

The molecular orbitals $\chi_p(\vec{\mathcal{E}})$ are defined as an expansion in terms of an atomic orbital basis set $|\underline{\xi}\rangle$:

$$\chi_p(\vec{\mathcal{E}}) = |\underline{\xi}\rangle\underline{C}_p(\vec{\mathcal{E}}). \tag{10}$$

From Eqs. (6)–(9) it follows that

$$F(\vec{\mathcal{E}})\Phi_0(\vec{\mathcal{E}}) = W_0(\vec{\mathcal{E}})\Phi_0(\vec{\mathcal{E}}), \tag{11}$$

where

$$\Phi_0(\vec{\mathcal{E}}) = \mathcal{A}[\chi_1(1)\cdots\chi_n(n)], \tag{12}$$

$$W_{\mathrm{CHF}}(\vec{\mathcal{E}}) = W_0(\vec{\mathcal{E}}) + \langle\Phi_0|V(\vec{\mathcal{E}})|\Phi_0\rangle. \tag{13}$$

In the CHF case, the SCF equations are solved for fixed (finite field) values of the field strength $\vec{\mathcal{E}}$. From these solutions, the CHF energy may be obtained as a function of $\vec{\mathcal{E}}$ as

$$W_{\mathrm{CHF}}(\vec{\mathcal{E}}) = \sum_{i=1}^{N}\epsilon_i(\vec{\mathcal{E}}) - \tfrac{1}{2}\sum_{i,j=1}^{N}\langle\chi_i(\vec{\mathcal{E}})\chi_j(\vec{\mathcal{E}})\|\chi_i(\vec{\mathcal{E}})\chi_j(\vec{\mathcal{E}})\rangle. \tag{14}$$

The double-bar notation designates the two-electron integral,

$$\langle\chi_p\chi_q\|\chi_r\chi_s\rangle = \int d\tau_1\int d\tau_2\,\chi_p^*(1)\chi_q^*(2)r_{12}^{-1}(1-P_{12}) \times\chi_r(1)\chi_s(2). \tag{15}$$

The CHF polarizabilities and hyperpolarizabilities may be derived from second and higher derivatives of $W_{\mathrm{CHF}}(\vec{\mathcal{E}})$ with respect to the field strength. Alternatively, the induced dipole moment can be calculated from the wave function, Eq. (12), with the polarizability and hyperpolarizabilities obtained as first, second, and higher derivatives of the induced dipole moment. The rigorous equivalence between the dipole procedure and the energy-based procedure depends upon the satisfaction of the Hellman-Feynman theorem for the approximate wave functions.[22]

As an alternative to the CHF model, a perturbation expansion of $F(\vec{\mathcal{E}})$ and $u(\vec{\mathcal{E}})$ in powers of $\vec{\mathcal{E}}$ may be made. This procedure, subject to orthonormality of the molecular orbitals, leads to the coupled perturbed Hartree-Fock (CPHF) method.[34-36] The results of CPHF and CHF are formally the same.[11]

In order to go beyond the CHF level and include

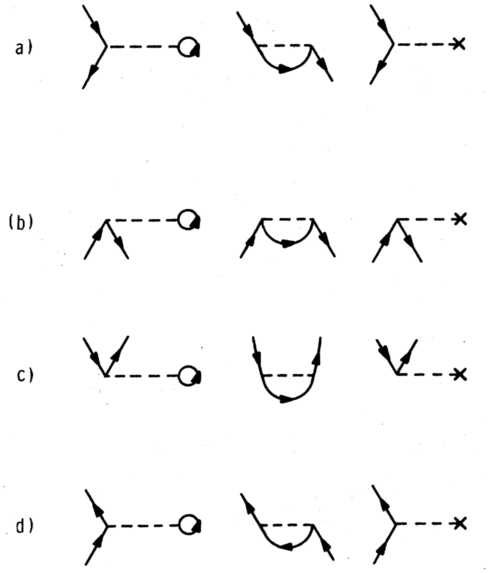

FIG. 1. Single-particle corrections to the energy diagrams. (---×) is the negative of the Fock potential. If occupied and excited one-particle orbitals are determined as SCF solutions at any field strength, then these diagrams component mutually cancel.

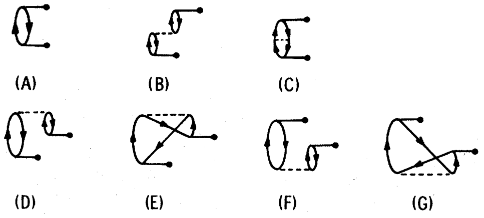

FIG. 2. Zeroth- and first-order relaxation diagrams for a second-order property. These terms are all included in a CHF calculation for a second-order property.

effects of correlation, the perturbation $V(\vec{\mathcal{E}})$ of Eq. (6) needs to be considered in more detail. Including this perturbation, the energy for the perturbed molecule can be obtained from the linked-diagram expansion[24] as

$$W(\vec{\mathcal{E}}) = W_{\mathrm{CHF}}(\vec{\mathcal{E}}) + \sum_{k=1}^{\infty} \langle\phi_0 | V(\vec{\mathcal{E}})[W_0(\vec{\mathcal{E}}) - F(\vec{\mathcal{E}})]^{-1} V(\vec{\mathcal{E}})]^k | \phi_0\rangle_L \,. \tag{16}$$

The terms defined by the summation in Eq. (16) are said to be the correlation corrections to the energy for a given field strength. Just as in the zero-field case, by solving the SCF equations in the presence of the field as in Eqs. (8)–(10), the SCF cancellations shown in Goldstone-diagram form in Fig. 1 (--- × is the negative of the Fock potential) are still maintained, so that no diagrams containing these parts are required.

The coefficients in Eq. (1) are given as derivatives of $W(\vec{\mathcal{E}})$ with respect to field strength. In the finite-field approach, $W(\vec{\mathcal{E}})$ must be computed for several field strengths to allow the determination of the polarizabilities, which requires taking small differences between large terms. If the differentiation is made initially, separate linked-diagram expansions for $\vec{\mu}$, $\vec{\alpha}$, $\vec{\beta}$, $\vec{\gamma}$, etc., in terms of the zero-field SCF orbitals $[\chi_p(0) = \chi_p^0,\ \epsilon_p(0) = \epsilon_p^0]$, can be used to evaluate the small polarizabilities directly.

In the latter case, ordinary double perturbation theory gives

$$W = W_0 + \sum_{k=0}^{\infty} \langle\Phi_0 | (V + \lambda\Omega) \times [(W_0 - F_0)^{-1} P (V + \lambda\Omega - \Delta W)]^k | \Phi_0\rangle \tag{17}$$

and, for some component $\mathcal{E}_x$,

$$W(\mathcal{E}_x) = W_0 + (W_{1,0} + W_{1,1} + W_{1,2} + \cdots)\mathcal{E}_x + (W_{2,0} + W_{2,1} + W_{2,2} + \cdots)\mathcal{E}_x^2 + \cdots, \tag{18}$$

$$W(\mathcal{E}_x) = W_{0,\infty} + W_{1,\infty}\mathcal{E}_x + W_{2,\infty}\mathcal{E}_x^2 + W_{3,\infty}\mathcal{E}_x^3 + \cdots. \tag{19}$$

Considering a second-order property for illustration, with the definition

$$R_0 = P(W_0 - F_0)^{-1} P, \tag{20}$$

where P is the projector for the orthogonal complement to Φ_0,

$$W_{2,\infty}(E_x) = \tfrac{1}{2}\alpha_{xx} = \langle\Phi_0 | x R_0 x | \Phi_0\rangle + \langle\Phi_0 | x R_0 (x - W_{1,0}) R_0 V | \Phi_0\rangle + \langle\Phi_0 | V R_0 (x - W_{1,0}) R_0 x | \Phi_0\rangle + \langle\Phi_0 | x R_0 (V - W_{0,1}) R_0 x | \Phi_0\rangle + \cdots. \tag{21}$$

The first term on right in Eq. (21), $W_{2,0}$, is given by the uncoupled Hartree-Fock (UCHF)[17] approximation [Fig. 2(A)], which is

$$W_{2,0} = \sum_{i(\mathrm{occ})} \sum_{a(\mathrm{unocc})} \frac{\langle\chi_i^0 | x | \chi_a^0\rangle}{\epsilon_i^0 - \epsilon_a^0}, \tag{22}$$

while the higher terms involve the field-independent perturbation $V(0)$. The Goldstone diagrams for second order in an external field and for zeroth and first order in the two-electron perturbation $V(0)$ are shown in Fig. 2. The symbol (---●) indicates interaction with the external field.

It is important to recognize that even though diagrams (B)–(G) of Fig. 2 involve a two-electron vertex, these diagrams and selection of others in all higher orders in $V(0)$ *are included*[27,34] in the

CHF results or in the perturbation-theory-equivalent CPHF.[35,36] At least in the static case these terms should *not* be considered as correlation corrections. These terms arise, instead, from the effective Fock potential $u(i)$, now written in terms of perturbed orbitals, which reflects the *relaxation* of the orbitals to the external perturbation.[34] Beyond first order in $V(0)$, additional diagrams arise which are *not* included in CPHF,[34,37] and these terms constitute true correlation corrections. In the finite-field approach, all terms which arise from derivatives of the summation in Eq. (16) are actual correlation corrections, while the initial CHF calculation provides the zeroth- and first-order energy corrections, subject to the field-dependent orbitals. (CPHF is the static equivalent of time-dependent Hartree-Fock theory or the random-phase approximation, which is similarly recognized to sum selections of many-body propagator diagrams to all orders.[38,39] In the time-dependent context, the terms so summed are frequently referred to as "dynamic" correlation.[39])

Even though the direct determination of the polarizabilities is a distinct advantage, it offers the disadvantage that separate sets of programs must be written to evaluate the diagrams for each order in the external perturbation, while the finite-field method allows *all* polarizabilities to be obtained from simply executing "enough" energy calculations at a series of field strengths. This also permits one to exploit the theories and programs that have been developed for the usual correlation problem[25] which typically offer a much more sophisticated level of treatment for the correlation than would be convenient to develop for each individual order in an external perturbation. Also, the dichotomy into correlation and relaxation effects is transparent for the finite-field method.

IV. NUMERICAL RESULTS

In the finite-field methods, it is necessary to obtain the various polarizability components from formulas for the energy or dipole moment. In the present work, either procedure may be used at the CHF level, since $\Phi_0(\vec{\mathcal{E}})$ satisfies the Hellman-Feynman theorem, but derivatives of $W(\vec{\mathcal{E}})$ will be used for the correlation corrections. By considering Eq. (1), it may be shown that the finite-difference formulas listed in Table I hold for the various polarizabilities. Each of these formulas is obtained by excluding all even or odd terms in Eq. (1) by using positive and negative field strengths of the same magnitude. This ensures that the contamination from the next higher term in the power series is completely removed, leaving only the next higher term of the same type (i.e., even or odd), which is about four orders of magnitude smaller (at the field strengths used here) than any polarizability being determined. Hence, essentially no error is anticipated from higher polarizability contamination. At the same time, however, field strengths of adequate size must be used to ensure that significant energy differences are obtained. In this work field strengths of 0.0, 0.01, and 0.02 a.u. are found to be suitable.

The formulas in Table I are general, but if some symmetry is present, formulas I.3 and I.6 become much simpler. If the molecule has a rotation axis, with i representing the direction of this axis, and j is perpendicular to i, group-theoretical considerations show that the components, β_{iij}, α_{ij}, γ_{ijjj}, and γ_{jiii} are vanishing at zero field strength. This results in particularly simple formulas for

TABLE I. Energy formulas for finite-field calculations of dipole moments, polarizabilities, and hyperpolarizabilities.[a]

Odd order

$$\mu_i\mathcal{E}_i = -\tfrac{2}{3}[W(\mathcal{E}_i) - W(-\mathcal{E}_i)] + \tfrac{1}{12}[W(2\mathcal{E}_i) - W(-2\mathcal{E}_i)] + O(\delta) \qquad (1)$$

$$\beta_{iii}\mathcal{E}_i^3 = \tfrac{1}{2}[W(2\mathcal{E}_i) - W(-2\mathcal{E}_i)] + [W(\mathcal{E}_i) - W(-\mathcal{E}_i)] + O(\delta) \qquad (2)$$

$$\beta_{jji}\mathcal{E}_j^2\mathcal{E}_i - \beta_{iij}\mathcal{E}_j\mathcal{E}_i^2 = -[W(\mathcal{E}_i - \mathcal{E}_j) - W(-\mathcal{E}_i + \mathcal{E}_j)] + [W(\mathcal{E}_i) - W(-\mathcal{E}_i)] - [W(\mathcal{E}_j) - W(-\mathcal{E}_j)] + O(\delta) \qquad (3)$$

Even order

$$\alpha_{ii}\mathcal{E}_i^2 = +\tfrac{5}{2}W(0) - \tfrac{4}{3}[W(\mathcal{E}_i) + W(-\mathcal{E}_i)] + \tfrac{1}{12}[W(2\mathcal{E}_i) + W(-2\mathcal{E}_i)] + O(\epsilon) \qquad (4)$$

$$\gamma_{iiii}\mathcal{E}_i^4 = +4[W(\mathcal{E}_i) + W(-\mathcal{E}_i)] - [W(2\mathcal{E}_i) + W(-2\mathcal{E}_i)] - 6W(0) + O(\epsilon) \qquad (5)$$

$$\tfrac{1}{2}\gamma_{iijj}\mathcal{E}_i^2\mathcal{E}_j^2 - 2\alpha_{ij}\mathcal{E}_i\mathcal{E}_j - \tfrac{1}{3}(\gamma_{jiii}\mathcal{E}_i^3\mathcal{E}_j + \gamma_{ijjj}\mathcal{E}_j^3\mathcal{E}_i) = -[W(\mathcal{E}_i - \mathcal{E}_j) + W(-\mathcal{E}_i + \mathcal{E}_j)] + [W(\mathcal{E}_i) + W(-\mathcal{E}_i)] + [W(\mathcal{E}_j) + W(-\mathcal{E}_j)] - 2W(0) + O(\epsilon) \qquad (6)$$

[a] For a molecule with a rotation axis in the direction i, α_{ij}, β_{iij}, γ_{jiii}, and γ_{ijjj} will be zero by symmetry.

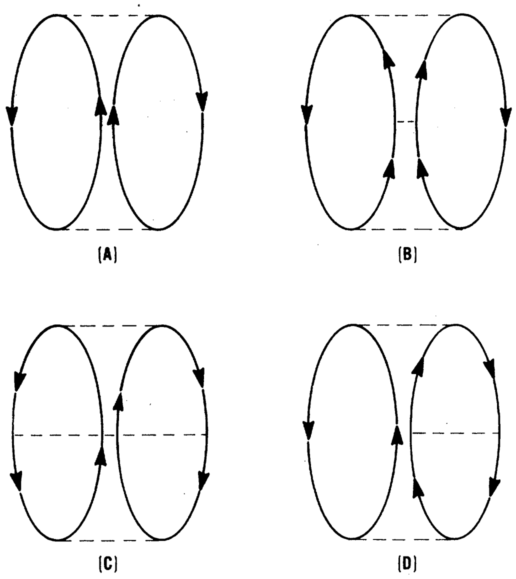

FIG. 3. All second- and third-order correlation diagrams provided that SCF (CHF) orbitals are used for the occupied and excited one-particle states. Antisymmetrized vertices are assumed in these diagrams.

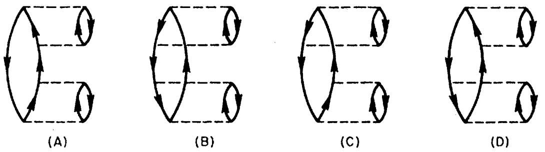

FIG. 4. All single-excitation fourth-order diagrams provided that SCF (CHF) orbitals are used for the occupied and excited one-particle states. Antisymmetrized vertices are assumed.

the nonvanishing components.

The finite-field correlation corrections included are shown as antisymmetrized diagrams in Figs. 3–6, where it is understood that the hole and particle lines are field dependent (or "dressed") and that finite differences of these quantities must be taken before the polarizabilities are obtained. (See Refs. 27 and 40 for the rules and algebraic formulas corresponding to these antisymmetrized diagrams.)

These diagrams consist of *all* terms that occur through fourth-order in the correlation, subject to field-dependent SCF orbitals that would arise due to configuration-interaction (CI) single, double, and quadruple excitations.[25] Triple excitations also contribute in the fourth-order energy, but these are excluded.

It is well known that CI-type single excitations are quite important in determining properties other than the energy, since operators such as $\vec{\mathscr{E}} \cdot \vec{r}$, will mix single excitations directly with an SCF unperturbed wave function. In the present work, the predominant effect of single excitations is introduced by means of the initial CHF calculations, which, as described in Sec. III, is responsible for summing a series of diagrams involving such single-excitation vertices as occur in Fig. 2 (i.e., ) to all orders. This "dresses" the hole and particle lines involved in Figs. 3–6. The remaining single excitations accounted for by Fig. 4 involve the smaller effect of single excitations of

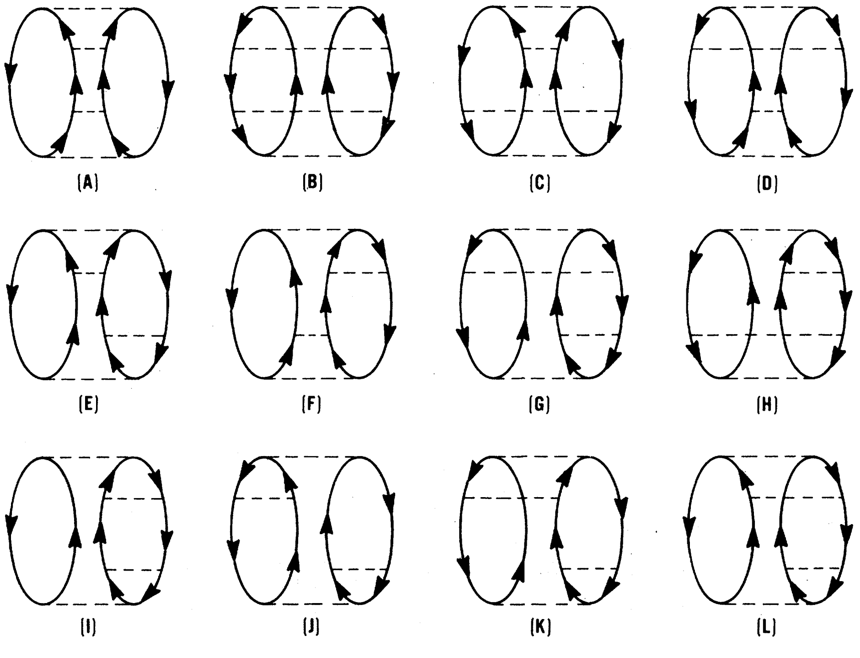

FIG. 5. All double-excitation fourth-order diagrams provided that SCF (CHF) orbitals are used for the occupied and excited one-particle states. Antisymmetrized vertices are assumed.

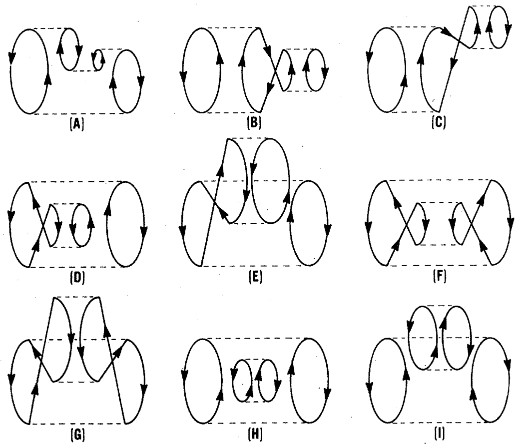

FIG. 6. All quadruple-excitation fourth-order diagrams, provided that SCF (CHF) orbitals are used for occupied and excited one-particle states. Unlinked diagrams (H) and (I) do not contribute to the correlation energy. Antisymmetrized vertices are assumed.

dressed lines that enter into the fourth-order energy only by interacting through dressed double excitations. The very high-order coupling of the first category of single-excitation effects with correlation due to double and quadruple diagrams by using "dressed" hole and particle lines is one of the additional advantages of the finite-field-based methods.

The basis set for the present study of HF is chosen essentially following the prescription of Christiansen and McCullough (CM).[19] We start from Dunning's[41] $5s3p$ contraction of Huzinaga's[42] $9s5p$ basis set for flourine, and Dunning's $3s$ contraction for hydrogen Slater exponent 1.2. These functions are augmented by a two-Gaussian fit to a d-STO for F with exponent 3.358, and a two-Gaussian fit to a p-STO, exponent 2.082 for H.[43] This results in a $5s3p1d/3s1p$ initial basis set. This basis is then augmented in a "well-tempered" fashion. The smallest exponent for each l quantum number per atom is multiplied by 0.4 to obtain a new, diffuse function to assist in describing the polarizability. The resulting basis $6s4p2d/4s2p$ is expected to be adequate to describe the dipole polarizability. To also attempt to account for the higher polarizabilities, the new exponent is again multiplied by 0.4 to add another p and d function on F, and an s and p function on H. Finally, the most diffuse d exponent on F was again multiplied by 0.4 and this function added to the basis set. We also consider the addition of an extra diffuse s function on F and the exclusion of the most diffuse s and p on H and the d function on fluorine. This provides four different basis sets.

A GTO basis set similar to these has been shown to account for the numerical CHF results for μ_z, α_{zz}, β_{zzz}, and γ_{zzzz} to within a few percent.[19] However, those authors were unable to reduce the error in the CGTO value for β_{zzz} below 7%. When we attempted to use their basis set, with all six possible Cartesian components of the d functions, xx, yy, zz, xz, yz, xy (CM use only the five normal d-function components), we found an approximate linear dependency which made our correlated calculations unstable. We were able to resolve this problem and also substantially reduce the error in the SCF β_{zzz} component by choosing a tighter d-polarization function on F (STO $\xi = 3.358$ compared to $\xi = 2.25$ for CM) and then adding an additional diffuse d function to the F atom. Both the tight and diffuse d functions seem to be important as illustrated in Table II. Using a tight d function while excluding the most diffuse d-function (bases A and B) results in a β_{zzz} that differs from the numerical result by 11%. In the CM basis, which has a very diffuse d function but excludes a tight polarization d function, a similar error in β_{zzz} occurs. By combining both, as in bases C and D, this error is greatly reduced.

The difference between bases C and D is the

TABLE II. Comparison of CHF results for HF in various basis sets with numerical CHF. ($R = 1.7328$ bohrs; values in a.u.)

Basis set (GTO)	$W(0)$	μ [a]	α_{zz}	β_{zzz}	γ_{zzzz}
CM ($6s5p3d/4s3p$) [b]	−100.0535	0.759	5.80	−9.0	310
A ($6s5p3d/5s3p$) [c]	−100.0563	0.757	5.72	−9.3	250
B ($7s5p3d/5s3p$) [c]	−100.0563	0.757	5.72	−9.2	260
C ($6s5p4d/4s2p$) [c]	−100.0563	0.759	5.73	−8.4	250
D ($6s5p4d/5s3p$) [c]	−100.0565	0.758	5.76	−8.5	280
Numerical CHF [b]	−100.0706	0.756	5.76	−8.3	320

[a] Coordinate system is chosen such that dipole moment (F^-H^+) is positive.

[b] Results of Ref. 16.

[c] Basis sets A, B, C, and D use all six Cartesian Gaussian d-orbital functions xx, yy, zz, xy, yz, and xz.

TABLE III. Effect of correlation and basis set on predicted dipole moment, polarizability, and hyperpolarizabilities of HF. (R=1.7328 bohrs; values in atomic units.)

		CHF				SDQ-MBPT(4)				
	CM[a]	A[b]	B[c]	C[d]	D[e]	A[b]	B[c]	C[d]	D[e]	Expt.
$W(0)$	−100.0535	−100.0563	−100.0563	−100.0563	−100.0565	−100.3030	(−100.3287)[f]	−100.3061	−100.3035	(−100.386)[g] (−100.448)[h,g]
W_{corr}	···	···	···	···	···	−0.247	(−0.272)[f]	−0.250	−0.247	(−0.315)[i] (−0.377)[j]
μ	0.759	0.7568	0.7569	0.7585	0.7580	0.7076	0.7082	0.7097	0.7089	(0.707)[k]
$\alpha_{zz}=\alpha_{\parallel}$	5.80	5.72	5.72	5.73	5.76	6.35	6.31	6.32	6.39	···
$\alpha_{yy}=\alpha_{xx}=\alpha_{\perp}$	···	4.45	4.45	4.51	4.48	5.13	5.11	5.22	5.18	···
$\alpha=\frac{1}{3}(\alpha_{zz}+\alpha_{yy}+\alpha_{xx})$	···	4.87	4.87	4.92	4.89	5.54	5.51	5.59	5.58	(5.52)[l]
$(\alpha_{\parallel}-\alpha_{\perp})$	···	1.27	1.27	1.22	1.28	1.22	1.20	1.10	1.21	(1.32)[l,m]
β_{zzz}	−9.0	−9.3	−9.2	−8.4	−8.5	−11.0	−10.8	−9.2	−9.7	···
$\beta_{zxx}=\beta_{zyy}$	···	−0.4	···	0.0	0.0	−1.2	···	0.6	0.6	···
$\beta=(\beta_{zzz}+\beta_{zxx}+\beta_{zyy})$	−10.1	···	−8.4	−8.5	−8.5	−13.3	···	−10.4	−10.9	···
γ_{zzzz}	130	250	260	250	280	350	350	340	390	···
γ_{yyzz}	···	70	···	80	80	130	···	130	140	···

[a] ($6s5p3d/4s3p$). Basis of Ref. 16.

[b] ($6s5p3d/5s3p$). Most diffuse s and d on F is excluded. Correlation calculations freeze F($1s^2$) electrons and drop the five highest-lying excited orbitals.

[c] ($7s5p3d/5s3p$). Most diffuse d on F excluded. All electrons are correlated and no excited orbitals are dropped.

[d] ($6s5p4d/4s2p$). Most diffuse s on F and diffuse s,p on H excluded. F($1s^2$) frozen and highest virtual orbitals dropped in correlated calculations.

[e] ($6s5p4d/5s3p$). Diffuse s on F excluded. F($1s^2$) frozen and highest virtual orbitals dropped in correlated calculations.

[f] All electrons are correlated.

[g] P. E. Cade and W. M. Huo, J. Chem. Phys. 47, 614 (1965), corrected for an estimated −0.082 relativistic energy and modified to exclude correlation involving the F($1s^2$) core electrons.

[h] Total nonrelativistic energy including the F($1s^2$) contribution.

[i] Valence correlation energy. SCF limit result is −100.0706 (Ref. 16).

[j] Total correlation energy.

[k] J. S. Mounter and W. Klemperer, J. Chem. Phys. 52, 6033 (1970).

[l] Reference 18. Corrected for zero-point vibration as in this reference.

[m] J. S. Mounter, J. Chem. Phys. 56, 5409 (1972).

TABLE IV. Contributions of different diagrams to dipole moment, polarizability, and hyperpolarizabilities of HF. (Basis set D; $R=1.7328$ bohrs; values in atomic units.[a])

				Fourth order				
				Single	Double	Quad.		
	CHF	Second order	Third order	Ex. Diam.	Ex. Diam.	Ex. Diam.	Total	SDQ-MBPT(4)	CHF + SDQ-MBPT(4)
$W(0)$	−100.056 47	−0.244 80	+0.001 56	−0.002 41	−0.003 47	+0.002 05	−0.003 83	−0.247 06	−100.303 53
μ_z	0.758 0	−0.047 8	+0.007 2	−0.005 8	−0.005 1	+0.002 4	−0.008 5	−0.049 1	0.708 9
$\alpha_{zz}=\alpha_{\parallel}$	5.76	+0.688	−0.230	+0.123	+0.079	−0.026	+0.176	+0.63	6.39
$\alpha_{yy}=\alpha_{\perp}$	4.48	+0.826	−0.332	+0.145	+0.080	−0.014	+0.206	+0.70	5.18
β_{zzz}	−8.48	−0.72	+0.49	−0.7	−0.4	+0.13	−0.97	−1.2	−9.7
$\beta_{yyz}=\beta_{xxz}$	−0.03	−0.64	+0.51	−0.3	−0.2	+0.03	−0.47	−0.6	−0.6
$\beta=(\beta_{zzz}+\beta_{yyz}+\beta_{xxz})$	−8.54	−2.0	+1.51	−1.3	−0.8	+0.20	−1.90	−2.4	−10.9
γ_{zzzz}	280	110	−60	50	20	−10	+60	120	390
γ_{yyzz}	80	60	−30	20	10	0	30	60	140

[a] Correlation involving the core is not included.

exclusion of the most diffuse s and p functions on H. This is seen to have almost no effect on β while having a somewhat larger effect on γ_{zzzz}. The observation that the diffuse H s and p functions have only a small effect is partially due to the fact that the diffuse region of the charge cloud is already accounted for by the other highly diffuse functions on F. However, γ_{zzzz} is usually larger the more diffuse functions that are included in the basis, as supported by the results of bases sets C and D.

It is clear from Table II that good agreement with the numerical results for μ_z, α_{zz}, β_{zzz}, and γ_{zzzz} can be achieved with the present basis sets. It does not necessarily follow that the other components of $\vec{\alpha}$, $\vec{\beta}$, and $\vec{\gamma}$ are as well described or that this basis is entirely adequate for the correlation corrections to the polarizabilities, but the good agreement with the numerical results for the parallel components at least provides an indication that the final correlation corrections to the different polarizabilities should be indicative of the size of the true correlation corrections, which is the primary objective of this study.

In the present correlated calculations, all the single, double, and quadruple excitation diagrams that arise through fourth order in the $V(\vec{\mathcal{E}})$ perturbation are included. This model will be referred to as SDQ-MBPT(4). These diagrams are evaluated at various field strengths, from which the equations of Table I are used to provide the different polarizabilities.

To carry out such finite-field calculations successfully, it is necessary to ensure about eight-decimal-place accuracy in all computations, from the initial molecular integrals to the actual diagram evaluation. The current computations employ the MBPT program system developed at Battelle.[44] Results for the effect of correlations on various properties are shown in Table III.

The $6s5p4d/5s3p$ basis set is seen to be capable of providing about 78% of the observed field-free valence-shell correlation energy. This is consistent with other calculations, where we have shown that a $5s3p1d/3s1p$ basis typically accounts for three-quarters of the valence-shell correlation energy.[25,45] since the remaining functions in the current bases are generally too diffuse to contribute much to the field-free correlation effect. On the other hand, correlation involving the normal *and* diffuse functions is important in the presence of the field, so some balance between a reasonable description of the valence-shell correlation and the long-range tails of orbitals is still expected to be significant in obtaining good correlated results for polarizabilities.

The effects of correlation on the other properties listed in Table III vary from about 7% for the dipole moment to 12% for the polarizability, and a rather dramatic change of about 22% for the β hyperpolarizability. A similarly large change is observed for the γ_{zzzz} component of the hyperpolarizability of 30%. The correlated dipole moment and polarizability are found to be in excellent agreement with experiment, although the anisotropy is somewhat farther away. The hyperpolarizabilities seem to be significantly affected by correlation, and although this is only a single molecule out of many, it suggests that a theoretical approach that attempts to predict and explain the experimental values for hyperpolarizabilities must definitely take into account the effects of correlation.

In Table IV are listed the individual correlation corrections for HF which are of some interest in answering questions about the order of perturbation theory needed to get converged correlated answers as well as the effect of the different types of diagrams. It is apparent that most of the correlation correction is obtained from just the second-order energy diagrams. In fact, a comparison of the second-order results with the SDQ-MBPT(4) values demonstrates that there is not too much change due to the third- and fourth-order diagrams, which are of opposite sign. In general, the fourth-order terms have a somewhat larger magnitude than third order, further augmenting the second-order result. This is particularly true of β_{zzz}. This behavior has also been observed in studies of molecular correlation energies,[25] as illustrated currently by $W(0)$ for the HF molecule. At first sight, this may cause some reservations, but comparison[25] between the DQ-MBPT(4) model for the correlation energy with the infinite-order sum of double and quadruple excitation diagrams normally known as the coupled-cluster-doubles (CCD)[28] model shows agreement to within a millihartree for a large group of atoms and molecules. Hence even though fourth order is larger than third order for this example, it does not necessarily follow that higher-order terms will be important. However, the very small differences involved in finite-field calculations might be more likely to be affected by higher-order terms; hence this question should be borne in mind. We will resolve this point in future work.

For each property except the energy, the single-excitation diagrams provide a larger fourth-order contribution than the double-excitations, while the quadruple excitations are typically a factor of 2 to 3 smaller than the fourth-order double-excitation contribution. This reflects the residual importance of single-excitation terms for properties dependent upon one-electron operators, even though this type of single-excitation contribution only appears (because of Brillouin's theorem) in the fourth-order energy via their coupling through double excitations. The predominant single-excitation effect, as discussed previously, is included at the CHF level. Triple-excitation diagrams also occur in fourth order and are likely to be somewhat more important than the quadruple excitations. These probably provide a correction with the same sign as the fourth-order single- and double-excitation diagrams. The relative unimportance of the quadruple excitations plus the fact that the quadruple and triple excitations should have an opposite effect on a polarizability suggest that a limitation to single- and double-excitation diagrams possibly summed to all orders should provide reliable results for these properties, if a well-chosen, well-balanced basis set is used.

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