Vol. A57 (1980) ACTA PHYSICA POLONICA No 6

CORRELATION CORRECTIONS TO THE HARTREE-FOCK PERTURBATION THEORY OF ATOMIC AND MOLECULAR PROPERTIES. DIPOLE POLARIZABILITIES OF He, Be AND Ne*

By A. J. Sadlej

Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw**

(Received October 30, 1979)

The problem of the most efficient perturbation calculation of the correlation contributions to atomic and molecular properties is discussed. The method which is based on the coupled Hartree-Fock (CHF) perturbation theory appears to be the most promising one. The CHF-based perturbation theory of correlation effects is applied to the calculation of the second-order correlation contributions to the electric dipole polarizabilities of He, Be and Ne. The numerical approach employed in this paper consists in computing first the electric-field-dependent SCF functions. Then, the field dependent second-order correlation energy is calculated. The electric dipole polarizabilities, accurate through the second-order in correlation, are obtained via the numerical differentiation of the field-dependent energies with respect to the external electric field strength. In order to avoid the use of very large basis sets the so-called electric-field-variant (EFV) orbitals are employed in the present study. The CHF results obtained in this paper are of the same accuracy as the best literature data. On addition of the second-order correlation correction the final values of the electric dipole polarizability differ from the accurate or experimental results by less than a few per cent.

1. *Introduction*

In spite of a variety of very promising and successful applications [1–5] of the coupled Hartree–Fock perturbation theory [6–10] to the calculation of electric and magnetic properties of many-electron systems [1, 2, 11] it is obvious that the theory needs to be corrected for the electron correlation effects. Fortunately enough the correlation errors of the CHF results are most frequently relatively small [2, 12–14]. However, in some cases [11–17] the electron correlation effects can be of ultimate importance.

The correlation effects can be accounted for either variationally by using appropriately selected form of the approximate wave function [12, 16, 18–22] or perturbationally [23–26]. As already mentioned, the correlation corrections to the CHF values of atomic and mole-

---

* This work was supported by the Institute of Low Temperatures and Structure Research of the Polish Academy of Sciences under contract No. MR-I.9.4.3.

** Address: Instytut Chemii Organicznej PAN, Kasprzaka 44, 01-224 Warszawa 42, Poland.

cular properties are usually fairly small. Thus, one can anticipate that the perturbation methods are perfectly suited for this purpose.

The perturbation theory of the correlation corrections to the CHF results has recently been discussed in detail by the present author [27]. The most important features of this theory will be briefly surveyed in Section 2. It has been pointed out previously [27, 28] that the CHF-based perturbation theory of the electron correlation effects should be quite efficient numerically already in relatively low orders with respect to the correlation perturbation. To illustrate this point we have performed the appropriate calculations for the electric dipole polarizability of He, Be and Ne. The computational methods used in the present study are described in Section 3 and the results are discussed in Section 4. A summary and conclusions with regard to the method employed in this paper will be presented in Section 5.

2. *Correlation corrections to the n-th order perturbed CHF energies*

Let $H^{(0)}$ be the total electronic Hamiltonian of a given unperturbed many-electron system

$$H^{(0)} = \sum_i f^{(0)}(i) + \sum_{i<j} r_{ij}^{-1}, \tag{1}$$

where the first term represents the one-electron part and the second operator refers to electron-electron repulsion. The perturbation by some external field of the strength μ,

$$\mu H^{(1,0)} = \mu \sum_i f^{(1)}(i), \tag{2}$$

is assumed to be of one-electron character [11]. The total Hamiltonian of the perturbed system becomes then

$$H = H(\mu) = H^{(0)} + \mu H^{(1,0)}, \tag{3}$$

so that the exact solutions of the Schrödinger equation

$$H(\mu)\Psi(\mu) = E(\mu)\Psi(\mu) \tag{4}$$

are μ-dependent [11, 29].

The notion of the correlation effects has its origin in the application of the Hartree–Fock (HF) approximation to the exact solution $\Psi(\mu)$. Let us suppose therefore that we know the HF solution corresponding to the Hamiltonian (3), i.e.

$$H_{\mathrm{HF}}(\mu)\Psi_{\mathrm{HF}}(\mu) = E_{\mathrm{HF}}(\mu)\Psi_{\mathrm{HF}}(\mu), \tag{5}$$

where $\Psi_{\mathrm{HF}}(\mu)$ is the μ-dependent many-electron HF wave function of a given perturbed system and

$$H_{\mathrm{HF}}(\mu) = \sum_i h(i; \mu) + C(\mu) \tag{6}$$

is the μ-dependent many-electron HF Hamiltonian [30–32]. The constant $C(\mu)$ [31] is determined by the condition that $E_{\mathrm{HF}}(\mu)$ represents the total HF energy of the perturbed system for $h(i; \mu)$ being the one-electron μ-dependent HF operators

$$h(i; \mu) = f^{(0)}(i) + \mu f^{(1)}(i) + v(i; \mu), \tag{7}$$

where $v(i;\mu)$ denotes the μ-dependent HF potential for the i-th electron [30]. The HF wave function $\Psi_{\mathrm{HF}}(\mu)$ is expressed in terms of μ-dependent spinorbitals $u_\alpha(i;\mu)$ which follow from the solution of the HF equations

$$h(i;\mu)u_\alpha(i;\mu) = e_\alpha(\mu)u_\alpha(i;\mu). \tag{8}$$

On expanding these equations in a power series in μ [6–10] one obtains the well-known perturbation equations of the CHF theory.

Owing to the introduction of the HF approximation the total Hamiltonian (3) can be partitioned in the following way

$$H = H(\mu, v) = H_{\mathrm{HF}}(\mu)+vH^{(1)}(\mu), \tag{9}$$

where

$$H^{(1)}(\mu) = \sum_{i<j} r_{ij}^{-1} - V_{\mathrm{HF}}(\mu) - C(\mu) \tag{10}$$

and

$$V_{\mathrm{HF}}(\mu) = \sum_i v(i;\mu). \tag{11}$$

The operator (10) represents the inaccuracy of the μ-dependent HF approximation and is referred to as the μ-dependent correlation perturbation. The corresponding perturbation parameter v has only a formal significance [33] and allows for the v-expansion of the exact perturbed energy

$$E(\mu) = E(\mu, v) = \sum_{m=0}^{\infty} v^m \bar{E}^{(m)}(\mu), \tag{12}$$

where $\bar{E}^{(m)}(\mu)$, $m \geqslant 1$, is the m-th order μ-dependent correlation correction to the HF energy $E_{\mathrm{HF}}(\mu) = \bar{E}^{(0)}(\mu)$.

By using the Brueckner–Goldstone "linked cluster" expansion formula [24, 34–36] we can define $\bar{E}^{(m)}(\mu)$ as

$$\bar{E}^{(m)}(\mu) = \langle \Psi_{\mathrm{HF}}(\mu)|H^{(1)}(\mu)\,(R_{\mathrm{HF}}(\mu)H^{(1)}(\mu))^{m-1}|\Psi_{\mathrm{HF}}(\mu)\rangle_{\mathrm{L}} \qquad m = 1, 2, \dots \tag{13}$$

where

$$R_{\mathrm{HF}}(\mu) = \frac{1}{H_{\mathrm{HF}}(\mu)-E_{\mathrm{HF}}(\mu)} \tag{14}$$

and L means that only the "linked" [34–36] terms are to be included in the diagrammatic expansion of Eq. (13). It is worth attention that in contrast to the standard form of the m-th order correlation correction [36, 37] the diagrammatic expansion of Eq. (13) will involve the μ-dependent hole and particle lines [27, 38], i.e. the hole and particle states which follow from the solution of the μ-dependent HF equations (8). However, the general form of the correlation energy diagrams [24, 36, 37] remains the same as in the case of the μ-independent problem [38].

Obviously, the final goal of the perturbation treatment of Eq. (4) is the calculation of the n-th order perturbed energies $E^{(n)}$ which are defined by the following expansion

$$E = E(\mu) = \sum_{n=0}^{\infty} \mu^n E^{(n)} = \sum_{n=0}^{\infty} \mu^n E^{(n)}(v). \tag{15}$$

The exact n-th order perturbed energies are the quantities which can be directly related to what is called the n-th order atomic and molecular properties [11]. As indicated in the r.h.s. of Eq. (15) these energies depend formally on the correlation perturbation (10). Thus, the total perturbed energy $E = E(\mu) = E(\mu, \nu)$ can be alternatively expanded in the double-perturbation series

$$E(\mu, \nu) = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \mu^n \nu^m \bar{E}^{(n,m)}, \tag{16}$$

where $\bar{E}^{(n,m)}$ is referred to as the m-th order correlation correction ($m \geqslant 1$) to the n-th order perturbed energy ($n \geqslant 1$) [31]. Since

$$\bar{E}^{(m)}(\mu) = \sum_{n=0}^{\infty} \mu^n \bar{E}^{(n,m)} \tag{17}$$

we obtain from Eq. (13) the following general formula

$$\bar{E}^{(n,m)} = \frac{1}{n!} \left[\frac{\partial^n}{\partial \mu^n} \bar{E}^{(m)}(\mu) \right]_{\mu=0}. \tag{18}$$

Its diagrammatic expansion has already been analysed and was shown to involve solely the so-called true correlation effects. The self-consistency effects (the apparent correlation effects) are completely accounted for at the HF level [27, 39], i.e. they contribute to the n-th order perturbed CHF energies $\bar{E}^{(n,0)} = E_{\mathrm{CHF}}^{(n)}$ which follow from the expansion of the μ-dependent HF energy

$$E_{\mathrm{HF}}(\mu) = E_{\mathrm{HF}}^{(0)} + \sum_{n=1}^{\infty} \mu^n E_{\mathrm{CHF}}^{(n)}. \tag{19}$$

The perturbation theory of the correlation effects can also be developed with reference to the HF approximation for the unperturbed system [23, 24, 31, 40]. Then, however, what should be called the m-th order correlation correction will in general involve simultaneously both the apparent correlation effects (i.e. the self-consistency effects) and the true correlation contributions [27]. The absence of the former ones in Eq. (18) for $m \geqslant 1$ shows that the present theory is developed at the HF level for both the unperturbed and the perturbed system. A detailed discussion of this problem has already been presented in our previous paper [27].

It is of note that the CHF-based perturbation theory of the correlation contributions as formulated in this paper suggests also a convenient computational scheme for the calculation of $E_{\mathrm{CHF}}^{(n)}$ and $\bar{E}^{(n,m)}$. Obviously, one can in principle use what is called the analytic approach and calculate directly all the diagrams which contribute to these energies. Far more convenient, however, is a completely numerical approach based on Eqs. (5), (8) and (18). It means that in the first step of our calculations we must calculate the field-dependent HF orbitals, i.e. the HF orbitals which follow from the HF equations for some selected numerical values of the field strength μ. The next step consists in calculating the correlation energies (13) by using the μ-dependent HF functions. Finally, the analytic differentiation with respect to μ is replaced by the numerical evaluation of the appropriate derivatives of $E_{\mathrm{HF}}(\mu)$ and $\bar{E}^{(m)}(\mu)$. This will give the n-th order CHF energies and the m-th order correlation corrections to them.

The numerical scheme outlined here follows the so-called finite-field perturbation methods [12, 13, 16, 32, 41, 42]. Although these methods are certainly not as elegant as the analytic schemes based on the appropriate spectral expansions [6–10, 21, 24, 39], they are definitely more convenient from the computational point of view. It should be pointed out that on using the numerical approach one can virtually employ the standard programs which are used for unperturbed calculations.

So far, the theory was developed under the assumption that the exact, i.e. the HF solutions of Eq. (8) are available. The practical calculations are, however, performed by using the finite basis set approximation, so that the correlation corrections are computed relative to the SCF perturbed energies. Furthermore, the finite SCF bases are also employed for the calculation of diagrammatic contributions to Eq. (13) [43–46]. The difference between the HF and the SCF functions can be accounted for e.g. perturbationally [47, 48]. However, it becomes of minor importance for large bases which are necessary in highly accurate calculations [47]. For this reason the present finite basis set (SCF) calculations will be identified with the HF data.

According to previously reported analysis of the CHF-based perturbation method for the calculation of the correlation corrections to $E^{(n)}_{\text{CHF}}$ it is expected that most of the correlation effects should be recovered already for relatively small values of m. It is of note that within the present formulation

$$\bar{E}^{(n,1)} \equiv 0 \tag{20}$$

for any value of n. This is the result of the HF approximation used for both the unperturbed and the perturbed system [25, 27, 28]. Thus, the first nonvanishing corrections will be of the second-order in correlation.

It follows from our previous preliminary studies [25, 28] that $\bar{E}^{(n,2)}$ should account for the major portion of the correlation corrections to $E^{(n)}_{\text{CHF}}$. This conclusion has also been supported by the analysis [27] of the recent numerical data of Itagaki and Saika [40]. Thus, the calculations reported in this paper are restricted to $m = 2$ and computing $\bar{E}^{(n,2)}$ means the calculation of the appropriate derivative of the lowest correlation energy diagram [25, 27, 38]. The theory is applied to the calculation of the second-order correlation corrections to the electric dipole polarizabilities of He, Be and Ne and the corresponding computational details are considered in the next section.

3. Second-order correlation corrections to the CHF polarizabilities. Methods of calculation and computational details

The electric dipole polarizability tensor corresponds to the system response to the external perturbation by a static homogeneous electric field in the second-order with respect to the field strength. For spherically symmetric systems the average dipole polarizability can be defined as [11]

$$\alpha = -2E^{(2)}, \tag{21}$$

where the exact second-order energy $E^{(2)}$ is calculated for some arbitrary direction of the external electric field. Similarly, in the CHF approximation one obtains

$$\alpha^{(0)} = \alpha_{\text{CHF}} = -2E_{\text{CHF}}^{(2)} = -2\bar{E}^{(2,0)} \tag{22}$$

while the second-order correlation correction to α_{CHF} is given by

$$\alpha^{(2)} = -2\bar{E}^{(2,2)}. \tag{23}$$

According to the discussion presented in the previous section it is expected that

$$\alpha \cong \alpha^{(0)}+\alpha^{(2)}. \tag{24}$$

As already mentioned, the present calculations have been carried out by using the finite basis set approximation. This approximation is fairly standard in the case of the CHF method [7–10]. Moreover, it has also proved to be quite reliable for the calculation of the ordinary correlation energies by using the many-body perturbation theory approaches [43–46, 49–52]. On computing the correlation corrections to the CHF polarizabilities the basis set requirements become, however, far more severe; a given basis set must simultaneously account for both the electric field perturbation [12, 13, 53, 54] and the correlation perturbation. It is already in the case of the CHF scheme that in order to obtain the electric dipole polarizabilities close to the corresponding HF limits one has to employ quite large bases [12, 13, 54]. Their further extension is likely to be necessary when computing the appropriate correlation corrections.

The problem of the basis set choice can be to some extent circumvented by using the functional bases which depend explicitly on the external electric field strength [55, 56]. The basic idea behind this approach is that the basis set size is kept the same for both the unperturbed and the electric-field-perturbed system. The electric field introduces some inherent modification of the analytic form of the basis set functions. In the case of Gaussian bases the pertinent modification was deduced by the consideration of the electric-field--perturbed harmonic oscillator problem [55].

Suppose that the unperturbed system is properly described at the SCF HF level by the M-dimensional basis set $\{\chi_1(\boldsymbol{r}; \alpha_1, 0), \chi_2(\boldsymbol{r}; \alpha_2, 0), \ldots, \chi_M(\boldsymbol{r}; \alpha_M, 0)\}$, where α_i denotes the orbital exponent and 0 means that the electric field strength $F = \mu$ is equal to zero. Since we shall deal with atomic systems the direction of the external electric field is completely arbitrary and F can be assumed e.g. to represent the field strength along the z axis. The so-called electric-field-variant (EFV) basis set is obtained from the set $\{\chi_i(\boldsymbol{r}; \alpha_i, 0)\}$ by making each basis function explicitly dependent on the electric field strength. In the case of GTO's the relevant EFV GTO bases are obtained by shifting the origin of each Gaussian towards the electric field direction by the amount which is proportional to the electric field strength and the inverse square of the orbital exponent [55, 56]. The shift is scaled by some parameter λ whose value is determined variationally through the minimization of the second-order CHF energy [57, 58]. Let us denote the optimum value of this parameter by $\hat{\lambda}$ [55–58]. Thus, the EFV GTO basis set which is optimized with respect to the CHF polarizability value can be represented by

$$\{\chi_i(\boldsymbol{r}; \alpha_i, \hat{\lambda}, F)\}. \tag{25}$$

Its size is exactly the same as that of the original GTO set and the parameter $\hat{\lambda}$ is assumed to be the same for all basis functions [55]. The CHF calculations performed with the aid of the EFV GTO functions have proved to be very efficient and accurate [59–61].

Once the parameter $\hat{\lambda}$ is evaluated one can calculate the field dependent SCF HF spinorbitals $u_\alpha(F, \hat{\lambda})$ (see Eq. (8)) by using the ordinary SCF methods [30, 32, 41, 57]. The virtual spinorbitals can be used then to compute the field-dependent second-order correlation energy $\bar{E}^{(2)}(F, \hat{\lambda})$. According to Eq. (13) we obtain a rather standard result [24, 36, 37, 62]

$$\bar{E}^{(2)}(F, \hat{\lambda}) = -\tfrac{1}{4} \sum_{i,j}^{\mathrm{occ}} \sum_{p,q}^{\mathrm{unocc}} \frac{1}{D_{pq,ij}(F, \hat{\lambda})}$$

$$\times |\langle u_i(1; F, \hat{\lambda}) u_j(2; F, \hat{\lambda}) | r_{12}^{-1}(1-P_{12}) | u_p(1; F, \hat{\lambda}) u_q(2; F, \hat{\lambda}) \rangle|^2, \tag{26}$$

where

$$D_{pq,ij}(F, \hat{\lambda}) = e_p(F, \hat{\lambda}) + e_q(F, \hat{\lambda}) - e_i(F, \hat{\lambda}) - e_j(F, \hat{\lambda}). \tag{27}$$

The correlation correction $\bar{E}^{(2,2)}(\hat{\lambda})$ follows then from the numerical differentiation of Eq. (26) with respect to F. The value of $\hat{\lambda}$ is assumed to be the same as that determined from the second-order CHF energy calculations. This completes a general description of the computational procedure employed in the present paper.

The use of the EFV GTO bases changes the strategy of the basis set choice. Since the external electric field effects are accounted for via the intrinsic modification of the original GTO set, one should only take care that a given GTO basis set provides a substantial portion of the second-order (field-independent) correlation energy. If so, one can expect that also the correction $\bar{E}^{(2,2)}(\hat{\lambda})$ can be predicted with satisfactory accuracy. It follows therefore that the calculations of $\alpha^{(2)}$ should be preceded by the qualification of the selected GTO bases with respect to the field-independent second-order correlation energy $\bar{E}^{(2)}(0, 0)$, i.e. the energy obtained from Eq. (26) for $F = \hat{\lambda} = 0$.

In the present paper the field-independent calculations have been carried out by using the GTO bases comprising s, p, and d orbitals. A complete description of these basis sets for He, Be and Ne is given in Table I. In general they have been constructed by augmenting the optimized GTO bases of van Duijneveldt [63] with some p and d orbitals whose exponents are shown in Table I. The influence of the basis set extension on the computed second-order correlation energy has been studied for He.

The field independent results for the total SCF energy and the second-order correlation energy are shown in Table I as well. They are compared with the so-called HF limits of the SCF energies [63, 64, 67] and the best available values of $\bar{E}^{(2)}(0, 0)$, respectively. The SCF energies calculated in this paper are very close to the corresponding HF limits and according to our previous conclusions [56, 60] one can expect that replacing the GTO's by the λ-optimized EFV GTO's should lead to near-HF values of electric dipole polarizabilities.

TABLE I

GTO basis sets for He, Be and Ne. Results of the field-independent calculations of the SCF energy (E_{SCF}) and the second-order correlation energy ($\bar{E}^{(2)}(0, 0)$). All energies in a.u.

Atom	Basis set	Contraction coefficients (orbital exponents)	E_{SCF}	$E^{(2)}(0, 0)$
He	(A)	s: $(10/5)^a$ p: 0.03429(15.0)+0.096302(5.5) +0.212006(2.13), 1.0(0.85), 1.0(0.343), 1.0(0.139) d: 1.0(1.0)	−2.861673	−0.03350
	(B)	s: $(10/5)^a$ p: 0.03429(30.56)+0.096302(11.05), 1.0(4.26), 1.0(1.70), 1.0(0.68), 1.0(0.277) d: 1.0(1.70), 1.0(0.68)	−2.861673	−0.03482
		Reference results	-2.861680^b	-0.03736^c
Be	(A)	s: $(13/7)^d$ p: 0.034842(134.447)+0.1058375(56.7443), 0.2460986(17.4427)+0.3867763(6.922), 1.0(2.904), 1.0(1.217), 1.0(0.5154), 1.0(0.2083), 1.0(0.0848) d: 0.2724444(0.5154)+0.2876675(0.0848), 1.0(0.2083)	−14.572954	−0.06659
		Reference results	-14.573022^b	-0.07629^c
Ne	(A)	s: $(13/7)^e$, 1.0(0.114065) p: $(8/4)^f$, 1.0(0.064715) d: 0.05665(24.346)+0.166455(8.946), 0.306363(3.5588)+0.365458(1.4462). 1.0(0.5863)	−128.541511	−0.2797
		Reference results	-128.54708^g	-0.3879^h

[a] 10s optimized set of van Duijneveldt [63] contracted to 5s set. Segmented contraction scheme: (6, 1, 1, 1, 1).

[b] Analytic SCF result close to the HF limit [64].

[c] The best literature value of the second-order correlation energy by Malinowski et al. [65]. See also Ref. [66].

[d] 13s optimized set of van Duijneveldt [63] contracted to 7s set. Segmented contraction scheme: (6, 2, 1, 1, 1, 1, 1).

[e] 13s optimized set of van Duijneveldt [63] contracted to 7s set. Segmented contraction scheme: (5, 2, 2, 1, 1, 1, 1).

[f] 8p optimized set of van Duijneveldt [63] contracted to 4p set. Segmented contraction scheme: (4, 2, 1, 1).

[g] Estimated HF limit [67].

[h] The best literature value of the second-order correlation energy by Jankowski et al. [68]. See also Refs. [69, 70].

The field-independent second-order correlation energies are, for obvious reasons, poorer than the best values reported in the literature [65, 66, 68–71]. Nonetheless in the case of He the set B recovers more than 90 per cent of the accurate value of $\bar{E}^{(2)}(0, 0)$. Nearly the same portion of the second-order correlation energy is also obtained for Be.

For both these atoms the difference between the present and the accurate values of $\bar{E}^{(2)}(0, 0)$ is mainly due to the neglect of higher than s-p and s-d excitations. The basis set employed in our calculations for Ne is relatively much smaller than those used for He and Be and gives only ca. 70 per cent of the accurate value of the field-independent second-order correlation energy. Using larger bases would be certainly desirable in the case of Ne. However, this would lead to a considerable increase of the computer time spent on the 4-index transformation of two-electron integrals. The basis set employed in the present study for Ne represents therefore a compromise between the accuracy of the computed second-order correlation energy and the corresponding computational effort.

The successive step of our calculations consists of the determination of the optimized value $\hat{\lambda}$ of the parameter λ which defines the EFV GTO bases. This parameter has been determined by the minimization of the λ-dependent second-order CHF energy $E^{(2)}_{\mathrm{CHF}}(\lambda)$ with respect to λ. The numerical technique used for this purpose has already been described in our previous papers [57, 61]. In all calculations reported in this paper the external electric field strength $F = 0.005$ a.u. has been used. This value is small enough so that $E_{\mathrm{HF}}(F, \hat{\lambda}) - E_{\mathrm{HF}}(0, 0)$ is only slightly contaminated by the higher than quadratic terms in F. Simultaneously, $F = 0.005$ is still large enough to make this difference numerically meaningful. The final results of the present EFV GTO calculations of the CHF polarizability of He, Be and Ne and the corresponding values of $\hat{\lambda}$ are presented in Section 4.

The field dependent SCF spinorbitals have been then recalculated for the optimized values of the parameter λ and used to evaluate the second-order correlation energy (26). As already mentioned its numerical differentiation with respect to F gives the second-order correlation correction to the CHF polarizability of a given system. The corresponding numerical results are shown in the next section.

4. *Results and discussion*

The results of the finite-field perturbation calculation of the CHF polarizabilities are summarized in Table II. Both the ordinary GTO ($\lambda = 0$) and the optimized EFV GTO ($\lambda = \hat{\lambda}$) results for the CHF polarizabilities are shown. They are compared with the best CHF results reported in the literature. This comparison clearly indicates a very high accuracy of the EFV GTO CHF scheme.

The second-order correlation corrections (23) calculated for $\lambda = \hat{\lambda}$ and the estimates of the total polarizability following from Eq. (24) are given in Table III. They are compared with the recommended (either experimental or theoretical) polarizability values which have recently been compiled by Miller and Bederson [72]. It can be seen that the estimate of the total polarizability as given by Eq. (24) is fairly close to the accurate values. It should be pointed out that the present finite GTO bases are not sufficiently large to give the accurate values of the second-order correlation energy $\bar{E}^{(2)}(0, 0)$. Thus, one can expect that on a further increase of the basis set size the correlation corrections to the CHF polarizabilities should also increase. This is illustrated by the data for He obtained with two different basis sets. The set (A) has been selected mostly by using the criteria appropriate for the CHF polarizability calculations. The second set (B) gives poorer value of the

TABLE II

CHF electric dipole polarizabilities of He, Be and Ne (in a.u.)[a]

Basis set	He		Be	Ne
	(A)	(B)	(A)	(A)
This work				
$\alpha_{\mathrm{CHF}}(0)$[b]	1.321	1.256	41.46	1.885
$\hat{\lambda}$[c]	0.0637	0.1397	0.1403	0.1184
$\alpha_{\mathrm{CHF}}(\hat{\lambda})$[d]	1.321	1.322	45.63	2.368
Best CHF[e]	1.32 [73]		45.63 [13]	2.368 [12]

[a] 1 a.u. of polarizability = 0.148185 Å^3 [74].

[b] Finite-field perturbation results obtained by using the field-independent GTO bases ($\lambda = 0$).

[c] Optimized value of λ for the appropriate EFV GTO bases derived from the basis sets of Table I.

[d] Finite-field perturbation results obtained by using the EFV GTO bases with $\lambda = \hat{\lambda}$.

[e] These are presumably the best CHF results obtained by using the field-independent basis sets. For other data see Refs. [12, 13, 75].

TABLE III

Results of the EFV GTO calculations of the second-order correlation correction to the CHF polarizability of He, Be and Ne. All data in a.u.[a]

Basis set	He		Be	Ne
	(A)	(B)	(A)	(A)
This work[b]				
$\alpha^{(2)}(\hat{\lambda})$	0.0372	0.0390	-6.16	0.190
$\alpha_{\mathrm{CHF}}(\hat{\lambda})+\alpha^{(2)}(\hat{\lambda})$	1.359	1.361	39.47	2.558
Recommended accurate value [72]				
α	1.38		37.8	2.67

[a] See Footnote a to Table II.

[b] Calculated for the optimized values of $\hat{\lambda}$ given in Table II.

λ-independent polarizability (Table II) but is more efficient with regard to the calculation of $\bar{E}^{(2)}(0, 0)$ (Table I). The optimization of λ for this basis set leads to near-HF value of the CHF polarizability and simultaneously increases the value of $\alpha^{(2)}(\hat{\lambda})$.

It is known that the whole of the polarizability of a given system is primarily defined by the contribution of the outer electronic shells. Thus, the second-order correlation corrections should also depend on the quality of a given basis set with respect to its ability to provide correct values of the second-order pair energies for outer shells. The second-

TABLE IV

Second-order pair correlation energies and the pair contributions to the second-order correlation correction to the CHF polarizability of Be and Ne

Atom	Pair contribution to[a]	Pair					
		(1s, 1s)	(1s, 2s)	(2s, 2s)	(1s, 2p)	(2s, 2p)	(2p, 2p)
Be	$\bar{E}^{(2)}(0, 0)$ This work	-0.03394	-0.00487	-0.02781			
	Accurate [65]	-0.04032	-0.00548	-0.03049			
	$\alpha^{(2)}(\hat{\lambda})$ This work	-0.90	-0.86	-4.40			
Ne	$\bar{E}^{(2)}(0, 0)$ This work	-0.01713	-0.00270	-0.00880	-0.01423	-0.05484	-0.18195
	Accurate [68]	-0.04022	-0.00556	-0.01202	-0.02217	-0.08715	-0.22080
	$\alpha^{(2)}(\hat{\lambda})$ This work	-0.009	-0.002	0.003	-0.014	0.038	0.173

[a] All data in a.u. For definitions see text.

-order pair energies calculated in this paper for Be and Ne are compared in Table IV with the most accurate data of Jankowski et al. [65, 68]. Also the pair contributions to the second-order corrections to the CHF polarizability are shown.

In the case of Be the inaccuracy of the present value of the field-independent pair energy for the outer (2s, 2s) pair amounts to less than 10 per cent. This result is similar to that obtained for the (1s, 1s) pair in He (see Table I). For Ne the second-order correlation correction to the CHF polarizability is mostly due to (2p, 2p) pairs. However, the basis set employed in this paper gives only ca. 80 per cent of the corresponding pair correlation energy. It is therefore expected that extending the basis set for Ne should result in higher values of the (2p, 2p) contribution to $\alpha^{(2)}(\hat{\lambda})$. Nonetheless, in spite of relatively small basis set the final estimate of α calculated in the present paper for Ne is only by ca. 4 per cent lower than the recommended value [72].

The conclusion that improving the $\bar{E}^{(2)}(0, 0)$ values by the appropriate selection of the basis set functions leads to the improvement of the total polarizability estimates according to Eq. (24) is also confirmed by our previous studies for the Be atom [25]. Virtually the same behaviour of the second-order correlation contribution of the CHF polarizability has also been calculated for the fluoride ion [28].

5. *Summary and conclusions*

The calculations reported in this paper provide the numerical illustration of our recent proposal concerning the calculation of the true correlation contributions to atomic and molecular properties [27]. According to the proposed computational scheme the CHF results are corrected for the correlation effects through the second-order in the correlation perturbation. Since the present method is based on the CHF approximation no pure-apparent correlation diagrams will enter the diagrammatic expansion for $\bar{E}^{(2,m)}$, $m \geqslant 1$. All the apparent correlation energy diagrams which have an open-chain structure [27, 39] are already accounted for at the CHF level.

The numerical calculations for He, Be and Ne indicate that the estimate of the accurate polarizability can be obtained according to Eq. (24). It means that for a variety of practical purposes, e.g. for the estimation of the long-range interaction energies [76, 77], the corresponding calculations can be reduced to the evaluation of Eq. (26) at some selected values of the external electric field.

It is suggested that all calculations should be performed by using the numerical finite-field perturbation approach [12, 13, 32, 41, 42]. This makes the computational scheme relatively simple; all calculations can be easily carried out by using the standard programs for the calculations of the SCF wave functions and the ordinary second-order correlation energies [24]. It should be also pointed out that the calculation of the higher-order correlation contributions can be performed in a similar way, i.e. by using the routines for the calculation of the higher-order correlation energies [52]. However, in comparison with the field-independent calculations a much higher accuracy is required in order to obtain meaningful results of the numerical differentiation of the field-dependent energies. Computing the higher-order correlation contributions to atomic and molecular properties calculated in the CHF approximation will be unavoidable if the HF approximation gives a rather poor estimate of the corresponding accurate values [78, 79].

The use of the 4-index transformation program prepared by Dr. M. Jaszuński is gratefully acknowledged.

REFERENCES

[1] W. N. Lipscomb, *Adv. Magn. Res.* **2**, 138 (1966).

[2] W. N. Lipscomb, in *MTP International Review of Science, Physical Chemistry. Series One. Theoretical Chemistry*, Eds. A. D. Buckingham, W. Byers Brown, vol. 1, p. 167.

[3] P. Lazzeretti, B. Cadioli, U. Pincelli, *Int. J. Quantum Chem.* **10**, 771 (1976); P. Lazzeretti, R. Zanasi, *J. Chem. Phys.* **68**, 832 (1978); P. A. Christiansen, E. A. McCullough, Jr., *Chem. Phys. Lett.* **63**, 570 (1979).

[4] T. Voegel, J. Hinze, F. Tobin, *J. Chem. Phys.* **70**, 1107 (1979); M. A. Morrison, P. J. Hay, *J. Chem. Phys.* **70**, 4034 (1979); R. L. Martin, E. R. Davidson, D. F. Eggers, Jr., *Chem. Phys.* **38**, 341 (1979).

[5] P. Swanstrøm, W. P. Kraemer, G. H. F. Diercksen, *Theor. Chim. Acta* **44**, 109 (1977); T. E. Raidy, D. P. Santry, *Chem. Phys. Lett.* **53**, 568 (1978).

[6] A. Dalgarno, *Adv. Phys.* **11**, 281 (1962) and references therein.

[7] R. M. Stevens, R. M. Pitzer, W. N. Lipscomb, *J. Chem. Phys.* **38**, 550 (1963).

[8] R. McWeeny, *Phys. Rev.* **126**, 1028 (1962).

[9] G. Diercksen, R. McWeeny, *J. Chem. Phys.* **44**, 3554 (1966).

[10] R. Moccia, *Theor. Chim. Acta* **8**, 8 (1967).

[11] D. W. Davies, *The Theory of the Electric and Magnetic Properties of Molecules*, J. Wiley, New York 1967.

[12] H.-J. Werner, W. Meyer, *Mol. Phys.* **31**, 855 (1976).

[13] H.-J. Werner, W. Meyer, *Phys. Rev.* **A13**, 13 (1976).

[14] G. H. F. Diercksen, B. O. Roos, A. J. Sadlej, *J. Chem. Phys.*, to be published.

[15] J. S. Sims, J. R. Rumble, Jr., *Phys. Rev.* **A8**, 2231 (1973).

[16] W. Meyer, in *Modern Theoretical Chemistry*, vol. 3, *Methods of Electronic Structure Theory*, Ed. H. F. Schaefer III, Plenum Press, New York 1977, p. 413 and references therein.

[17] R. M. Glover, F. Weinhold, *J. Chem. Phys.* **65**, 4913 (1976).

[18] W. Kołos, L. Wolniewicz, *J. Chem. Phys.* **46**, 1426 (1967).

[19] H. J. Kolker, H. H. Michels, *J. Chem. Phys.* **43**, 1027 (1965).
[20] F. P. Billingsley II, M. Krauss, *Phys. Rev.* **A6**, 855 (1972).
[21] M. Jaszuński, A. J. Sadlej, *Theor. Chim. Acta* **40**, 157 (1975); M. Jaszuński, A. J. Sadlej, *Int. J. Quantum Chem.* **11**, 233 (1977).
[22] K. Szalewicz, L. Adamowicz, A. J. Sadlej, *Chem. Phys. Lett.* **61**, 548 (1979).
[23] J. I. Musher, *J. Chem. Phys.* **46**, 369 (1967).
[24] H. P. Kelly, *Adv. Chem. Phys.* **14**, 129 (1969).
[25] L. Adamowicz, A. J. Sadlej, *Chem. Phys. Lett.* **53**, 377 (1978).
[26] T. Itagaki, A. Saika, *Chem. Phys. Lett.* **52**, 530 (1977).
[27] A. J. Sadlej, *J. Chem. Phys.*, submitted for publication.
[28] A. J. Sadlej, *J. Phys. Chem.* **83**, 1653 (1979).
[29] J. Killingbeck, *Rep. Prog. Phys.* **40**, 963 (1977).
[30] R. McWeeny, B. T. Sutcliffe, *Methods of Molecular Quantum Mechanics*, Academic Press, New York 1969.
[31] D. F.-T. Tuan, S. T. Epstein, J. O. Hirschfelder, *J. Chem. Phys.* **44**, 431 (1966).
[32] H. D. Cohen, C. C. J. Roothaan, *J. Chem. Phys.* **43**, S34 (1965).
[33] S. T. Epstein, in *Perturbation Theory and Its Applications in Quantum Mechanics*, Ed. C. H. Wilcox, J. Wiley, New York 1966, p. 49.
[34] K. A. Brueckner, *The Many-Body Problem*, J. Wiley, New York 1959.
[35] J. Goldstone, *Proc. Roy. Soc.* (London) **A239**, 267 (1957).
[36] D. J. Thouless, *The Quantum Mechanics of Many-Body Systems*, Academic Press, New York 1961.
[37] N. H. March, W. H. Young, S. Sampanthar, *The Many-Body Problem in Quantum Mechanics*, Cambridge University Press, Cambridge 1967.
[38] A. J. Sadlej, School on Computational Methods in Quantum Chemistry, Jabłonna n/Warsaw, May 1975, Lecture Notes.
[39] T. C. Caves, M. Karplus, *J. Chem. Phys.* **50**, 3649 (1969).
[40] T. Itagaki, A. Saika, *J. Chem. Phys.* **70**, 2378 (1979).
[41] J. A. Pople, J. W. McIver, N. S. Ostlund, *J. Chem. Phys.* **48**, 2960 (1968).
[42] J. E. Gready, G. B. Bacskay, N. S. Hush, *Chem. Phys.* **23**, 9 (1977).
[43] J. M. Schulman, D. M. Kaufman, *J. Chem. Phys.* **53**, 477 (1970).
[44] J. M. Schulman, D. M. Kaufman, *J. Chem. Phys.* **57**, 2328 (1972).
[45] U. Kaldor, *Phys. Rev.* **A7**, 427 (1973).
[46] U. Kaldor, *J. Chem. Phys.* **62**, 4634 (1975).
[47] A. J. Sadlej, *Mol. Phys.* **26**, 1445 (1973).
[48] K. McDowell. *J. Chem. Phys.* **68**, 4151 (1978); K. McDowell, *J. Chem. Phys.* **69**, 5050 (1978).
[49] R. J. Bartlett, D. M. Silver, *J. Chem. Phys.* **62**, 3258 (1975).
[50] S. Wilson, D. M. Silver, *J. Chem. Phys.* **66**, 5400 (1977).
[51] D. M. Silver, S. Wilson, R. J. Bartlett, *Phys. Rev.* **A16**, 477 (1977).
[52] S. Wilson, D. M. Silver, *Mol. Phys.* **36**, 1539 (1978); R. J. Bartlett, G. D. Purvis, *Int. J. Quantum Chem.* **14**, 561 (1978).
[53] V. P. Gutschick, V. McKoy. *J. Chem. Phys.* **58**, 2397 (1973).
[54] W. Meyer, *Chem. Phys.* **17**, 27 (1976).
[55] A. J. Sadlej, *Chem. Phys. Lett.* **47**, 50 (1977).
[56] A. J. Sadlej, *Acta Phys. Pol.* **A53**, 297 (1978).
[57] S. T. Epstein, A. J. Sadlej, *Int. J. Quantum Chem.* **15**, 147 (1979).
[58] J. L. Dodds, R. McWeeny, A. J. Sadlej, *Mol. Phys.* **34**, 1779 (1977).
[59] A. J. Sadlej, *Theor. Chim. Acta* **47**, 205 (1978).
[60] A. J. Sadlej, *Mol. Phys.* **34**, 731 (1977).
[61] A. J. Sadlej, *Mol. Phys.* **36**, 1701 (1978).
[62] I. Hubač, P. Čársky, *Topics in Current Chem.* **75**, 97 (1978).
[63] F. B. van Duijneveldt, *IBM J. Res. RJ* (1971) 943.

[64] E. Clementi, *IBM J. Res. Dev.*, Suppl. **9**, 2 (1965).
[65] P. Malinowski, M. Polasik, K. Jankowski, *J. Phys. B* **12**, 2965 (1979).
[66] E. Eggarter, T. P. Eggarter, *J. Phys. B* **11**, 1157 (1978),
[67] S. Huzinaga, D. McWilliams, B. Domsky, *J. Chem. Phys.* **54**, 2283 (1971).
[68] K. Jankowski, P. Malinowski, *Phys. Rev.* **A21**, 45 (1980).
[69] K. Jankowski, P. Malinowski, *Chem. Phys. Lett.* **54**, 68 (1978).
[70] E. Eggarter, T. P. Eggarter, *J. Phys. B* **11**, 2069 (1978).
[71] F. W. Byron, C. J. Joachain, *Phys. Rev.* **146**, 1 (1966); F. W. Byron, C. J. Joachain, *Phys. Rev.* **157**, 1, 7 (1967).
[72] T. M. Miller, B. Bederson, *Adv. Atom. Mol. Phys.* **13**, 1 (1978).
[73] R. R. Teachout, R. T. Pack, *Atomic Data* **3**, 195 (1971).
[74] E. R. Cohen, B. N. Taylor, *J. Phys. Chem. Ref. Data* **2**, 663 (1973).
[75] P. J. Fortune, P. R. Certain, *J. Chem. Phys.* **61**, 2620 (1974).
[76] A. D. Buckingham, *Adv. Chem. Phys.* **12**, 107 (1967).
[77] A. T. Amos, R. J. Crispin, in *Theoretical Chemistry. Advances and Perspectives*, Eds. H. Eyring, D. Henderson, Academic Press, New York 1976, vol. 2, p. 1.
[78] M. Jaszuński, B. O. Roos, *Chem. Phys. Lett.* **67**, 189 (1979).
[79] M. Jaszuński, A. J. Sadlej, to be published.