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Fourth-order many-body perturbation-theory study of the electron-correlation contribution to polarizabilities of Ne

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Different electric polarizabilities of Ne are calculated by using the complete fourth-order many-body perturbation-theory (MBPT) method and a partly optimized set of Gaussian-type orbital and contracted Gaussian-type orbital basis functions. The results obtained by the MBPT method (dipole polarizability $\alpha=2.712$ a.u., dipole hyperpolarizability $\gamma=104.6$ a.u., quadrupole polarizability $C=3.85$ a.u., dipole-quadrupole polarizability $B=-17.75$ a.u.) are considered as the best currently available theoretical estimates. The importance of the electron-correlation contribution is demonstrated by the comparison with the corresponding self-consistent-field Hartree-Fock results ($\alpha=2.374$ a.u., $\gamma=63.9$ a.u., $C=3.20$ a.u., $B=-12.75$ a.u.).

I. INTRODUCTION

During the past decade the problem of the electron-correlation contribution to electric properties of many-electron systems has been clearly recognized.[1-4] However, the corresponding numerical studies have been primarily carried out for the first- and second-order properties related to the perturbation by a homogeneous static electric field. Accurate data for the electron correlation contribution to either higher-order[2,5,6] or higher-multipole[4,7-10] electric properties of atoms and molecules are relatively rare. On the other hand those quantities enter into a variety of models for describing different atomic and molecular phenomena and processes[11-13] and their reliable theoretical values are of particular interest.

A systematic study of the different polarizabilities of Ne has recently been carried out by Maroulis and Bishop.[14] However, these authors have focused their attention on the accuracy of the calculated polarizabilities within the self-consistent-field Hartree-Fock (SCF-HF) approximation while completely neglecting the electron-correlation contribution. Certainly, for finite-basis-set SCF-HF calculations the basis-set choice is one of the major factors affecting the calculated results.[1,7,10,15,16] However, the accurate evaluation of the electron-correlation contribution is at least equally important.[1-10]

Our recent studies of different atomic and molecular properties[4,10] indicate that the many-body perturbation-theory (MBPT) approach[2-5,17,18] carried out through the fourth order with respect to the electron-correlation perturbation provides quite reliable estimates of the corresponding correlation contributions. In the present paper this method is applied to the calculation of accurate data for different polarizabilities of the Ne atom. Both the dipole polarizability (α) and the quadrupole polarizability (C) (Refs. 11 and 19) have been accurately computed in different previous studies[1,7,9,20,21] and our present results are included merely for the sake of completeness of this report. To our knowledge accurate data for the dipole hyperpolarizability (γ) and mixed dipole-quadrupole polarizability (B) (Refs. 11 and 19), including the electron-correlation contribution to these properties are not yet available.

Several computational aspects of the present study which are necessary for qualifying the accuracy and reliability of our results and a brief survey of the theory underlying the present calculations are given in Sec. II. Different MBPT correlation contributions to the polarizabilities of Ne are presented in Sec. III and followed by estimates of the corresponding correlation corrections. The discussion of our final results and the evaluation of their reliability are given in Sec. IV.

II. THEORY AND COMPUTATIONAL DETAILS

A. The MBPT series for correlation corrections to properties

The MBPT expansion for properties of many-electron systems has been thoroughly discussed in several recent papers[2-4,10,18] and only some basic concepts and definitions will be presented in this section. A more detailed account of the theory can be found in Refs. 3 and 4. Our notation closely follows that of Ref. 4.

The kth-order property Q is defined[11] as a quantity proportional to the kth-order derivative of the total perturbation-dependent energy $E(\mu)$ with respect to the perturbation strength μ:

$$Q \sim \left[\frac{\partial^k E(\mu)}{\partial \mu^k} \right]_{\mu=0} . \tag{1}$$

The generalization of this definition to more than one external perturbing field is quite obvious.[11] On expressing[3,4] the total energy as a sum of the SCF-HF value $E^{\mathrm{HF}}(\mu)$ and the correlation correction $E_{\mathrm{corr}}(\mu)$,

$$E(\mu)=E^{\mathrm{HF}}(\mu)+E_{\mathrm{corr}}(\mu)\ , \tag{2}$$

one obtains an analogous formulation for the electron correlation contributions to Q:

$$Q=Q^{\mathrm{HF}}+Q_{\mathrm{corr}}\ ,$$

where in general Q^{HF} corresponds to the value obtained by using the so-called coupled Hartree-Fock (CHF) perturbation theory.[3,22]

The MBPT expansion of the correlation energy $E_{\mathrm{corr}}(\mu)$ (Refs. 4, 17, and 18)

$$E_{\mathrm{corr}}(\mu)=E_2(\mu)+E_3(\mu)+E_4(\mu)+\cdots \tag{3}$$

can be further split into contributions due to different intermediate states which appear in the reduced resolvent operator,[17] i.e.,

$$E_2(\mu)=E_2^D(\mu)\ , \tag{4}$$

$$E_3(\mu)=E_3^D(\mu)\ , \tag{5}$$

$$E_4(\mu)=E_{4d}^S(\mu)+E_{4d}^D(\mu)+E_{4d}^T(\mu)+E_{4d}^Q(\mu)+E_{4r}^D(\mu)\ , \tag{6}$$

and according to (1) gives formally the same expansion for Q_{corr}:

$$Q_{\mathrm{corr}}=Q_2^D+Q_3^D+Q_{4d}^S+Q_{4d}^D+Q_{4d}^T+Q_{4d}^Q+Q_{4r}^D+\cdots\ . \tag{7}$$

The superscripts correspond to the type of intermediate states arising from single (*S*), double (*D*), triple (*T*), and quadruple (*Q*) orbital substitutions in the reference HF single determinant while the subscripts refer to the order of the correlation perturbation expansion and the type of contribution [direct (*d*) or renormalization (*r*) terms].[4,17] A more detailed description of symbols employed in the present paper is given in Ref. 4.

In atomic and molecular calculations the MBPT-correlation perturbation series is usually truncated at some finite order n and this leads to the nth-order approximation to Q_{corr}:

$$Q_{\mathrm{corr}}^{\mathrm{MBPT}}(n)=\sum_{i=2}^{n} Q_i \tag{8}$$

and the total Q value

$$Q^{\mathrm{MBPT}}(n)=Q^{\mathrm{HF}}+Q_{\mathrm{corr}}^{\mathrm{MBPT}}(n)\ , \tag{9}$$

where the superscript MBPT is used to indicate that all components of (7) through the nth order are rigorously included.[4] Several approximate methods based on the truncation of the reduced resolvent expansion[17] have also received some attention.[4,23–25] On neglecting in the energy expansion (3) the contribution of higher then doubly substituted states and all renormalization terms one obtains[24] what is known as the *SD*-MBPT approximation to Q_{corr}. Through the fourth order in the electron-correlation perturbation one has then

$$Q_{\mathrm{corr}}^{SD\text{-MBPT}}(4)=Q_2^D+Q_3^D+Q_{4d}^S+Q_{4d}^D \tag{10}$$

and

$$Q^{SD\text{-MBPT}}(4)=Q^{\mathrm{HF}}+Q_{\mathrm{corr}}^{SD\text{-MBPT}}(4)\ . \tag{11}$$

Neglecting only the contribution due to triply substituted intermediate states[2,5] gives the so-called *SDQ* approximation to $Q_{\mathrm{corr}}^{\mathrm{MBPT}}(4)$:

$$Q_{\mathrm{corr}}^{SDQ\text{-MBPT}}(4)=Q_{\mathrm{corr}}^{SD\text{-MBPT}}(4)+Q_{4d}^Q+Q_{4r}^D \tag{12}$$

and the corresponding approximation to Q,

$$Q^{SDQ\text{-MBPT}}(4)=Q^{\mathrm{HF}}+Q_{\mathrm{corr}}^{SDQ\text{-MBPT}}(4)\ . \tag{13}$$

To complete this survey of formulas and definitions let us mention the fourth-order *SD* approximation to the Rayleigh-Schrödinger perturbation series (RSPT) for Q_{corr}:

$$Q_{\mathrm{corr}}^{SD\text{-RSPT}}(4)=Q_{\mathrm{corr}}^{SD\text{-MBPT}}(4)+Q_{4r}^D\ , \tag{14}$$

which differs from Eq. (10) by the fourth-order renormalization term.[23–25] This term involves unlinked diagrammatic contributions[17,23,26] which are canceled out by the Q_{4d}^Q term in the MBPT expansion. Since Eq. (14) can be considered as the fourth-order perturbation approximation to the configuration-interaction scheme based on single and double substitutions (*SD*-CI) in the reference HF determinant, the Q_{4r}^D term gives an estimate of the incorrectness of the *SD*-CI result for the correlation contribution to Q (Ref. 27).

A more detailed discussion of different approximations to the correlation perturbation series for Q and the evaluation of their accuracy can be found in our previous papers.[3,4,10] A useful comparison of different MBPT and coupled-cluster techniques for the evaluation of electric properties has recently been given by Kucharski *et al.*[28]

The calculation of different terms in the expansion (7) follows from the definition (1) and in principle can be carried out analytically[3,29,30] through the evaluation of separated diagrammatic contributions. However, even for relatively low orders of the MBPT expansion the number of different diagrams becomes prohibitively large. For this reason in most MBPT studies of correlation contributions to Q the derivatives of the perturbation-dependent energy are evaluated numerically.[2–4] In the numerical finite-field approach the problem of the calculation of a very large number of different diagrammatic contributions to Q is replaced by the problem of the numerical accuracy which will be discussed in Sec. II C. Obviously, each of the two approaches offers some advantages and disadvantages and the choice depends mostly on the available computational environment.

The major problem of most calculations of atomic and molecular properties is, however, concerned with the use of what is called the algebraic approximation[31] for single-particle states which are approximated by an expansion into some finite set of basis functions.[31] The quality of the basis set is the major factor affecting the accuracy of both the SCF-HF and MBPT results[1–4] for properties. With the aim of a high accuracy of calculated properties the problem of the basis-set choice should be given particular attention and will be discussed in the next section.

B. The basis set choice and optimization

In the algebraic approximation the accuracy of the calculated atomic and molecular properties is determined to a large extent by the basis set flexibility and the amount of the electron-correlation effects which are accounted for by the given computational method.[1–4] The first factor is already quite important at the SCF-HF level of approximation[1] and in recent years several standardized solutions to the problem of the appropriate selection of the basis set functions have been given by different authors.[1,7,15,16,32–34] The calculated correlation corrections depend on the basis set choice as well,[1,3,4] and both the basis set size and flexibility require a careful consideration.[10,16]

In the SCF-HF approximation the basis set choice problem is not particularly difficult. Apart from the existence of several standardized recipes concerning both the type of atomic functions and their orbital exponents,[1,7,15,16] there is a possibility of their optimization according to different variation criteria for the calculated properties.[10,15,35]

A formal differentiation of the perturbation-dependent MBPT contributions to $E(\mu)$ shows that the calculation of correlation corrections to the SCF-HF value of the kth-order energy requires the knowledge of the perturbed single-particle states through the kth order.[3,4,10,36] Hence, the perturbed single-particle states optimized at the CHF level of approximation should be suitable for the evaluation of correlation corrections to the given property. This strategy of the basis set optimization[10,16] is followed in the present paper. Obviously, in addition to functions which provide near-HF values of properties in the SCF approximation the basis set must also comprise those functions which are responsible for recovering the major part of the correlation energy. Both these criteria are usually simultaneously satisfied by the recently devised method for the construction of the so-called polarized basis sets.[16]

The initial (s,p) basis set for Ne is the (13.8) set of Gaussian-type orbitals (GTO's) taken from the tabulation by van Duijneveldt,[39] contracted to 8 s-type and 5 p-type contracted Gaussian-type orbitals (CGTO's) and then extended by one diffuse s-type GTO and one set of diffuse p-type GTO's, leading to the [14.9/9.6] (s,p) CGTO subset. The orbital exponents of the diffuse functions have been selected by assuming that they are members of a geometric progression within each subset.

The set of 7 six-component d-type GTO's contracted to the corresponding 4 CGTO's has been obtained by the method of Ref. 16. Finally, 5 ten-component f-type GTO's contracted to 2 f-type CGTO's with the orbital exponents and contraction coefficients determined in a similar way as for the d subset[16] have been added, resulting in the [14.9.7.5/9.6.4.2] CGTO set of 71 functions. By the method of its determination[16] this basis set should be at least suitable for calculating the CHF values of α and C. Their values calculated with the present CGTO basis set are shown in Table I and compared with the presumably most accurate SCF-HF results of McEachran *et al.*[37] Taking into account that the method[16] used to produce the polarized CGTO basis set does not involve any optimization of orbital exponents, the corresponding results for α and C are quite satisfactory. However, for computing the MBPT-correlation corrections to polarizabilities one needs at least high-quality first-order perturbed orbitals and reasonably good higher-order single-particle functions. For this reason the d subset was partly decontracted and the f subset extended by one more set of ten diffuse functions with the orbital exponent selected accordingly to the method of Ref. 16. The dipole polarizability value obtained with the extended [14.9.7.6/9.6.5.3] GTO/CGTO basis set comprising 87 functions is in perfect agreement (Table I) with the corresponding reference value. The quadrupole polarizability C is, however, still a little too low, indicating that the quality of our basis set is not good enough for the accurate representation of the perturbation due to the external field gradient. In order to remedy this deficiency of the basis set we have carried out a straightforward optimization of orbital exponents in the f subset by using a common scaling factor. It follows from the symmetry of the perturbation operator[10,11] that the choice of orbital exponents in the f subset is mainly responsible for variations in the calculated value of C. On the other hand, the changes made in the f subset have a negligible effect on the SCF-HF dipole polarizability.

TABLE I. The GTO/CGTO basis set optimization with respect to the SCF-HF values of the dipole and quadrupole polarizabilities (in a.u.).

	SCF-HF polarizabilities[a]	
	α	C
This work		
[14.9.7.5/9.6.4.2]	2.322 (2.322)	3.109 (3.109)
[14.9.7.6/9.6.5.3]	2.374 (2.374)	3.173 (3.174)
[14.9.7.6/9.6.5.3][b]	2.375 (2.374)	3.196 (3.196)
Reference values[c]	2.377	3.211

[a] The present results follow from the numerical differentiation of either induced moments or (values in parentheses) field/field-gradient-dependent energies. See Sec. II C for details.

[b] Results with the f subset optimized with respect to C.

[c] Accurate CHF results of McEachran *et al.* (Ref. 37).

As shown by the data of Table I the optimized [14.9.7.5/9.6.5.3] GTO/CGTO set, which corresponds to multiplying all exponents of the initial f subset by 0.5, gives an excellent agreement with the reference value of the quadrupole polarizability C. This final basis set is given in Table II and was used in our MBPT calculations reported in Sec. III.

The technique employed in this paper for the derivation of a suitable basis set for the calculation of the relevant correlation contributions represents a combination of two approaches developed in our previous studies of atomic and molecular properties.[10,16] The method of construction of the initial GTO/CGTO basis set has been shown[16] to be appropriate for the description of the homogeneous electric field perturbation. An extension of the same

TABLE II. Partly optimized [14.9.7.6/9.6.5.3] GTO/CGTO basis set employed in MBPT calculations of polarizabilities of the Ne atom.

CGTO	GTO expansion $\sum_i c_i \chi^{\mathrm{GTO}}(\alpha_i)$
s subset	
1	0.000 047 (166 165.08)+0.000 401 (23 107.524) + 0.002 193 (5060.1539)+0.009 588 (1384.6123) + 0.035 074 (436.512 58)
2	0.104 652 (153.471 48)+0.237 716 (59.389 087)
3	1.0 (24.861 967)
4	1.0 (11.015 704)
5	1.0 (4.965 175)
6	1.0 (1.936 503)
7	1.0 (0.765 728)
8	1.0 (0.295 538)
9	1.0 (0.114 065)
p subset	
1	0.001 575 (234.945 00)+0.012 496 (55.077 385) + 0.056 650 (17.389 549)
2	0.166 455 (6.389 537)+0.306 363 (2.542 082)
3	1.0 (1.033 764)
4	1.0 (0.418 788)
5	1.0 (0.164 627)
6	1.0 (0.064 715)
d subset	
1	0.001 684 (55.077 385)+0.013 585 (17.389 549) + 0.065 851 (6.389 537)
2	1.0 (2.542 082)
3	1.0 (1.033 764)
4	1.0 (0.418 788)
5	1.0 (0.164 627)
f subset	
1	0.026 050 (3.194 769)+0.120 520 (1.271 041) + 0.353 520 (0.516 882)
2	0.696 840 (0.209 394)+0.535 590 (0.082 314)
3	1.0 (0.032 358)

method to perturbations by the field gradient would result in elliptic Gaussian functions[15] and require nonstandard integral packages. We found in our previous studies[10] that the orbital optimization is numerically more convenient though perhaps slightly less efficient.

Extensive SCF-HF calculations of polarizabilities of Ne have recently been carried out by Maroulis and Bishop.[14] Their best result for α is comparable with our value while our quadrupole polarizability is much closer to the result of McEachran *et al.*[37] We conclude therefore that our perturbed SCF-HF orbitals are closer to the corresponding exact singe-particle states and should be more appropriate for the calculation of both the SCF-HF and correlated values of polarizabilities.

The four polarizabilities of Ne considered in our paper have been calculated recently in the SCF-HF approximation by Fowler and Buckingham.[38] However, the GTO/CGTO basis set employed by these authors is of much poorer quality than those utilized in this paper.

C. Numerical finite-field calculations of polarizabilities

The major advantage of the numerical finite-field approach is that different properties can be obtained by using standard programs for calculations of energies and average values of different operators. The major disadvantage follows from the possible instabilities and inaccuracies of the numerical differentiation. This problem is particularly acute if the given method does not satisfy the Hellmann-Feynman theorem.[36] Then, the only legitimate way of calculating the kth-order property is by taking the kth-order derivative of the perturbation-dependent energy. The corresponding analytic expressions are usually quite difficult to handle[40] for $k \geq 2$. On the other hand, calculating the energy derivatives numerically for $k > 2$ may represent a formidable task because of accuracy requirements.

Under certain circumstances the order of the numerical differentiation can be lowered by using the $(k-1)$th derivatives of perturbation-dependent average values of operators corresponding to the appropriate first-order properties. This is the case of the SCF-HF method with perturbation independent basis sets.[40,41] In this case the kth-order polarizabilities can be calculated either as the kth-order energy derivatives or the $(k-1)$th-order derivatives of induced moments. For the MBPT method one has to use the energy-differentiation scheme.[40,41] However, the accuracy of these results can be checked to some extent by comparing the property values calculated in two different ways in the SCF-HF approximation. This check on the numerical accuracy of calculated polarizabilities is performed in the present paper.[10]

According to Buckingham[11] a spherically symmetric system embedded in the external electric field along the z direction with the strength equal to $F=F_z$ and the field gradient $V=V_{zz}=-2V_{xx}=-2V_{yy}$ will have the energy given by

$$E(F,V)=E(0,0)-\tfrac{1}{2}\alpha F^2-\tfrac{1}{24}\gamma F^4-\tfrac{1}{4}BF^2V-\tfrac{1}{4}CV^2-\cdots \quad (15)$$

The induced dipole and quadrupole moments are

$$\mu=\alpha F+\tfrac{1}{6}\gamma F^3+\tfrac{1}{2}BFV+\cdots \quad (16)$$

and

$$\Theta=\tfrac{1}{2}BF^2+CV+\cdots\ , \quad (17)$$

respectively. Assuming that the higher-order terms in Eqs. (15)–(17) can be neglected one can obtain the corresponding finite-difference approximations to α, γ, B, and C. This is usually a good approximation for $E(F,0)$, since then the next term is of the order of F^6 and for well-confined electron densities its contribution should be indeed small. However, in the case of $E(0,V)$ the contributions of the order V^3 and V^4 are not negligible. The same problem appears in the case of $\Theta(0,V)$.

In the case of SCF-HF calculations there are two ways of computing α and γ, i.e., the numerical differentiation of either $E(F,0)$ or $\mu(F,0)$. In the present paper the following finite difference expressions have been used.

Dipole polarizability:

$$\alpha=-\left[\frac{\partial^2 E(F,0)}{\partial F^2}\right]_{F=0}\simeq 2\frac{F_1^4[E(F_2,0)-E(0,0)]-F_2^4[E(F_1,0)-E(0,0)]}{F_1^2F_2^4-F_1^4F_2^2}\ , \quad (18a)$$

$$\alpha=\left[\frac{\partial \mu(F,0)}{\partial F}\right]_{F=0}\simeq\frac{F_1^3\mu(F_2,0)-F_2^3\mu(F_1,0)}{F_1^3F_2-F_1F_2^3}\ . \quad (18b)$$

Dipole hyperpolarizability:

$$\gamma=-\left[\frac{\partial^4 E(F,0)}{\partial F^4}\right]_{F=0}\simeq 24\frac{F_2^2[E(F_1,0)-E(0,0)]-F_1^2[E(F_2,0)-E(0,0)]}{F_1^2F_2^4-F_1^4F_2^2}\ , \quad (19a)$$

$$\gamma=\left[\frac{\partial^3 \mu(F,0)}{\partial F^3}\right]_{F=0}\simeq 6\frac{F_2\mu(F_1,0)-F_1\mu(F_2,0)}{F_1^3F_2-F_1F_2^3}\ , \quad (19b)$$

where F_1 and F_2 are two values of the external electric field strength selected in such a way that in the SCF-HF approximation the two schemes give nearly the same results for α and γ, respectively. The corresponding values of the field strength appropriate for α are found to be $F_1=0.002$ a.u. and $F_2=0.005$ a.u. Those values, however, are too small to produce meaningful energy changes in higher orders in F. The values of the electric field strength suitable for the calculation of the SCF-HF value of γ have been determined to be $F_1=0.01$ a.u. and $F_2=0.02$ a.u.

The SCF-HF quadrupole polarizability values can be obtained either from the energy differences

$$C=-2\left[\frac{\partial^2 E(0,V)}{\partial V^2}\right]_{V=0}$$

$$\simeq\frac{2}{V_1^2V_2^2(V_2^2-V_1^2)}\{V_1^4[E(0,V_1)+E(0,-V_1)-2E(0,0)]-V_2^4[E(0,V_2)+E(0,-V_2)-2E(0,0)]\}\ , \quad (20a)$$

or

$$C=\left[\frac{\partial \Theta(0,V)}{\partial V}\right]_{V=0}\simeq\frac{1}{2V}[\Theta(0,V_1)-\Theta(0,-V_1)]\ . \quad (20b)$$

Because of the above-mentioned contamination of $E(0,V)$ and $\Theta(0,V)$ it is necessary to use higher-order expansions of both these quantities. The two values of V in Eqs. (20) suitable for the calculation of C in the SCF-HF approximation have been found to be $V_1=0.002$ a.u. and $V_2=0.005$ a.u.

Three distinct numerical approximations can be used to obtain the SCF-HF results for the dipole-quadrupole polarizability B, i.e.,

$$B=-2\left[\frac{\partial^3 E(F,V)}{\partial F^2 \partial V}\right]_{F,V=0} \simeq \frac{2}{F^2 V}[E(F,V)-E(F,-V)-E(0,V)+E(0,-V)]\ , \tag{21a}$$

$$B=2\left[\frac{\partial^2 \mu(F,V)}{\partial F \partial V}\right]_{F,V=0} \simeq \frac{1}{FV}[\mu(F,V)-\mu(F,-V)]\ , \tag{21b}$$

and

$$B=\left[\frac{\partial^2 \Theta(F,0)}{\partial F^2}\right]_{F=0} \simeq \frac{2}{F^2}\Theta(F,0)\ . \tag{21c}$$

They give nearly the same values of B for $F=0.002$ a.u. and $V=0.005$ a.u.

The values of F and V determined at the SCF-HF level of approximation have been used then in calculations of different diagrammatic components of the perturbation-dependent MBPT energies. The resulting MBPT-correlation corrections to α, γ, C, and B have been obtained according to Eqs. (18a), (19a), (20a), and (21a), respectively.

In the present paper the perturbation parameters F and V are assumed to have some *direct* numerical values and the calcultaed quantities at least are not contaminated by contributions involving higher gradients of the external field. Such additional contamination effects will occur in principle if the perturbation is due to an inhomogeneous external field which can be produced by external charges. This form of the finite-field perturbation technique has been introduced long ago by McLean and Yoshimine[41] and recently revived by Maroulis and Bishop.[14] Because of the mentioned additional contaminations in comparison with our technique, the point-charge perturbation scheme may require more calculations of perturbed energies. The contamination effects are not likely to be important for spherically symmetric systems. However, we feel that for systems of lower symmetry the finite-field perturbation scheme pursued in our MBPT studies of electric properties[4,8–10] is computationally more efficient and credible.

III. MBPT CORRELATION CORRECTIONS TO THE POLARIZABILITIES OF Ne

Different electron-correlation corrections to the SCF-HF polarizabilities of Ne which occur in their MBPT expansions through the fourth-order with respect to the correlation perturbation, are listed in Table III. The unperturbed correlation energy values are also included, though they are of little interest for the present study. The reported results have been obtained with the partly optimized [14.9.7.6/9.6.5.3] GTO/CGTO basis set shown in Table II and by using the numerical scheme of Sec. II C. In all MBPT calculations the 1*s* electron pair has been left uncorrelated. This certainly affects the calculated correlation energy contributions. However, freezing the core electron pair in Ne has practically no effect on the calculated polarizabilities.

The correlation contributions to α and C which occur in the *SD* approximation to the fourth-order MBPT treatment have been calculated in our previous studies[9,42] with slightly less flexible basis sets. However, for both α and C the contributions Q_2^D, Q_3^D, $Q_{4d}^S+Q_{4d}^D$ and Q_{4r}^D obtained in this paper are close to our previous results.[9,42]

For all polarizabilities studied in this paper the major part of the electron-correlation contribution is accounted for by the second-order term Q_2^D. However, the higher-order contributions are not negligible. Their importance increases with the order of polarizability and indicates a

TABLE III. Correlation contributions to the energy and polarizabilities of Ne. All values in a.u.

			Property[b]		
Contribution[a]	E	α	γ	C	B
Q_2^D	−0.266 277	0.343	31.9	0.63	−4.54
Q_3^D	0.001 034	−0.112	−15.3	−0.23	1.74
Q_{4d}^S	−0.001 695	0.047	9.8	0.10	−0.91
Q_{4d}^D	−0.002 407	0.025	4.3	0.05	−0.41
Q_{4d}^T	−0.005 962	0.044	11.2	0.13	−1.02
$Q_{4d}^Q+Q_{4r}^D$	0.001 851	−0.008	−1.3	−0.02	0.14
Q_{4r}^D	0.009 438	−0.059	−7.5	−0.12	0.87
$Q_{4r,cj}^D$ [c]	0.004 635	0.020	128.3	0.04	0.34

[a] For definitions of symbols see Sec. II A.

[b] The polarizabilities are defined according to the conventions used by Buckingham (Ref. 11).

[c] The conjoint diagrammatic contribution to the fourth-order renormalization term (Refs. 4 and 23).

rather slow convergence of the MBPT series for higher-order electric properties. Of particular interest are the Q^{Q}_{4d} and the different renormalization contributions.[4,23,24] Although the sum $Q^{Q}_{4d}+Q^{D}_{4r}$ is small compared to other fourth-order terms, its components may have very large values. The data of Table III confirm our previous suggestions[24] that the conjoint part of the fourth-order renormalization term[4,23] should be completely neglected in the approximate MBPT schemes involving soley singly and doubly substituted intermediate states. Although the $Q^{D}_{4r,cj}$ term does not violate the linked cluster theorem[17] its presence has to be balanced by contributions from Q^{Q}_{4d}. Finally, let us also mention the relatively large magnitude of the Q^{S}_{4d} and Q^{T}_{4d} contributions to the polarizabilities.[4,10]

Different approximations to the total correlation contribution to both the energy and polarizabilities are given in Table IV together with estimates of the corresponding total values of Q. As already observed in our earlier atomic and molecular calculations the second-order MBPT scheme gives results for α and C which are very close to those obtained in the complete fourth-order treatment. The same pattern is observed also for the higher-order polarizabilities B and γ. The third-order results are, however, systematically lower than both $Q^{\text{MBPT}}(2)$ and $Q^{\text{MBPT}}(4)$. Approximate MBPT approaches based on *SD* and *SDQ* approximations give results relatively close to the complete fourth-order MBPT values of properties. On the other hand, the *SD*-RSPT approach understimates the magnitude of the correlation correction.[4,10] This feature of the fourth-order *SD*-RSPT approximation indicates that the *SD*-CI results for properties should be affected in a similar way.[4,27]

The general pattern of the present results for electric properties follows closely that observed and discussed in previous calculations.[2–6,8–10] From the formal point of view the complete fourth-order MBPT results should be considered as the most credible predictions. However, it follows from the slow convergence of the correlation corrections that the fourth-order approach still may not be sufficient. Performing complete higher than the fourth-order calculations with basis sets satisfying all requirements mentioned in Sec. II B is not feasible at the moment. The methods which are based on incomplete higher-order treatments and partial summations of certain classes of diagrams[18,28,43] are known[44,45] to destroy the subtle balance between different contributions and their credibility cannot be *a priori* qualified. From this point of view the highly systematic character of complete order-by-order MBPT calculations makes them certainly advantageous in comparison with other methods.

The only possible way of confirming the expected high accuracy of the complete fourth-order MBPT results is by a reference to experimental data. Unfortunately, the results for other than the dipole polarizabilities are very scarce and usually unreliable. Some comparisons, which are discussed in Sec. IV, seem to confirm the high quality and predictive value of our complete fourth-order MBPT results.

IV. SUMMARY AND DISCUSSION

The SCF-HF and fourth-order MBPT results for the polarizabilities of Ne calculated in the this paper are compared in Table V with the best available SCF-HF data of other authors and a few correlated values for α and C. The known experimental values of α and γ are also included. The value of α has been determined with very

TABLE IV. Approximations for correlation contributions and total correlated values of different properties of Ne. All data in a.u.

		Property[b]			
Approximation[a]	E	α	γ	C	B
Correlation corrections					
$Q^{\text{MBPT}}_{\text{corr}}(2)$	−0.266 277	0.343	31.9	0.63	−4.54
$Q^{\text{MBPT}}_{\text{corr}}(3)$	−0.265 243	0.230	16.6	0.40	−2.80
$Q^{\text{MBPT}}_{\text{corr}}(4)$	−0.273 456	0.338	40.7	0.66	−5.00
$Q^{SD\text{-MBPT}}_{\text{corr}}(4)$	−0.269 345	0.302	30.8	0.55	−4.12
$Q^{SDQ\text{-MBPT}}_{\text{corr}}(4)$	−0.267 494	0.294	29.5	0.53	−3.98
$Q^{SD\text{-RSPT}}_{\text{corr}}(4)$	−0.251 907	0.243	23.3	0.43	−3.25
Total					
$Q^{\text{SCF-HF}}$	−128.546 540	2.374	63.9	3.20	−12.75
$Q^{\text{MBPT}}(2)$	−128.812 817	2.717	95.8	3.82	−17.29
$Q^{\text{MBPT}}(3)$	−128.811 783	2.605	80.5	3.59	−15.55
$Q^{\text{MBPT}}(4)$	−128.819 996	2.712	104.6	3.85	−17.75
$Q^{SD\text{-MBPT}}(4)$	−128.815 885	2.674	94.6	3.74	−16.87
$Q^{SDQ\text{-MBPT}}(4)$	−128.814 034	2.668	93.4	3.72	−16.73
$Q^{SD\text{-RSPT}}(4)$	−128.798 447	2.617	87.2	3.63	−16.00

[a] For definitions of symbols see Sec. II A.

[b] All definitions of polarizabilities follow those of Ref. 11.

TABLE V. Comparison of theoretical and experimental data for polarizabilities of Ne. All values in a.u.

	Theoretical			
Property	This work		Reference results	Experimental
α	SCF-HF:	2.374	2.374,[a] 2.377,[b] 2.377,[c] 2.37,[d]	
	MBPT(4):	2.712	MBPT: 2.603,[e] 2.672,[f] 2.67[g] CEPA: 2.676[h]	2.663[i] 2.669[j]
γ	SCF-HF:	63.9	7×10^1,[a] 70,[d] 78,[d] 14.2[k]	
	MBPT(4):	104.6		101 ± 8[l] 118 ± 3[m] 95 ± 16[n]
C[o]	SCF-HF:	3.20	3.211,[p] 3.229,[q] 3.26,[r] 3.232,[s] 3.19,[t] 3.06[d]	
	MBPT(4):	3.85	MBPT: 3.208,[e] 3.74[u] CEPA: 3.86,[s]	
B	SCF-HF:	-12.75	-13.6,[d] -6.5964[k]	
	MBPT(4):	-17.75		

[a] Seminumerical SCF result of Ref. 33.
[b] Reference 37.
[c] Reference 46.
[d] Reference 14.
[e] Reference 47. See also comments in Refs. 9 and 42.
[f] Reference 48.
[g] *SD*-MBPT value of Ref. 42.
[h] Reference 1.
[i] Reference 49.
[j] Reference 50.
[k] Reference 38.
[l] Reference 51.
[m] Reference 52.
[n] Reference 53.
[o] C is half of the value of the quadrupole polarizability α_Q usually considered in atomic physics.
[p] Reference 37.
[q] Reference 54.
[r] Reference 55.
[s] Reference 7.
[t] Reference 9.
[u] *SD*-MBPT result of Ref. 9.

high accuracy[49,50] and can be used for checking the quality of the theoretical data. The experimental value of γ is definitely less certain.

As already mentioned the dipole and quadrupole polarizabilities of Ne have been accurately calculated by a number of different authors in both the SCF-HF and several other approximations which take into account the correlation effects. The present SCF-HF results for α are in excellent agreement with the corresponding data obtained from numerical SCF calculations.[33,46] Hence, one can conclude that the GTO/CGTO basis set employed in this paper is at least capable of providing sufficiently accurate first-order perturbed orbitals for the homogeneous electric field perturbation.

A similar comparison of our SCF-HF value of C with the presumably most accurate value of McEachran[37] indicates only a very small discrepancy. Thus, the first-order perturbed wave function for the field-gradient perturbation should also be quite acceptable.

Not too much, however, can be said about the quality of our higher-order perturbed orbitals which enter the formal analytic expansions for correlation corrections considered in this paper.[3,4,36] The second-order perturbed single-particle states enter the SCF-HF expression for γ and their quality might have been estimated by comparing our SCF-HF value with those of other authors.[14,38,46] However, the numerical SCF-HF result of Voegel *et al.*,[46] which in principle could be the HF limit for γ, has a rather low numerical accuracy. The results of Maroulis and Bishop[14] are higher than our value in spite of the more diffuse character of our basis set as compared to their (13.9.4.2) GTO set. The further extension and optimization of the *d*-subset which has been carried out by these authors is based on the minimization of the total energy of the Ne atom in the presence of a remote point charge. This may result in an artificially too diffuse basis set compared to that which would follow from the perturbed energy minimization, and thus, in overestimated values of γ. Moreover, the presence of very diffuse functions should be balanced by adding functions with very high orbital exponents.[35,39] Let us recall that from the point of view of the electric field perturbation our final basis set was derived by the method which guarantees a proper description of perturbation effects.[15,16]

Our value of B is also a little lower than the SCF-HF result of Maroulis and Bishop[14] although their value of C is rather far from the most accurate SCF-HF result.[37] The analytic calculation of B in the single-particle approximation would involve the first-order perturbed SCF orbitals for both the electric field and electric-field gradient perturbations. Since the latter perturbed states are better reproduced in our basis set, the value of B reported in this paper should be closer to the HF limit than that calculated by Maroulis and Bishop.

Some deviations from either estimated or expected HF limits for electric polarizabilities of Ne seem, however, to be rather immaterial because of the crucial role of correlation effects in determining the final property values. Although the SCF-HF results for α and C are not too far from the corresponding correlated values, it appears to be almost meaningless to substitute the exact values of higher-order properties by their HF counterparts, the correlation contribution to B amounts to about 30% while for γ nearly half of its value comes from the electron correlation effect. The same has already been observed in the case of the fluoride ion.[6]

Obviously, the present calculations give only *estimates* of the total correlation contribution to different properties. For α this estimate, which follows from the complete fourth-order treatment, is a little too high and our MBPT(4) value of α is 1—2 % larger than the accurate experimental value. Since the convergence of the MBPT series for γ is much slower than for α, the present MBPT(4) result for the dipole hyperpolarizability is presumably less accurate. In addition, our basis set is certainly not as good for MBPT calculations of γ as it is in the case of α.

We claim that the MBPT polarizabilities of Ne calculated in this paper are the *best theoretical estimates* obtained so far in calculations at the correlated level. This is achieved by the proper selection and partial optimization of the GTO/CGTO basis set[16] and a systematic study of correlation effects.[4] Obviously, a further extension and more complete optimization of the basis set functions will affect the results. In particular, the higher-order polarizabilities γ and B. Extending the MBPT treatment to higher-orders would also affect the results for correlation corrections. It must be clearly stated that due to incomplete basis sets and the limitation of the correlation-perturbation expansion to relatively low order, one cannot expect to compute the exact values of properties. If the calculated data are equal to the exact (experimental) values it means that either (i) there is a fortuitous cancellation of different inaccuracies, or (ii) the neglected basis set and correlation effects are negligibly small, or (iii) the reference data are not accurate enough for legitimate comparisons. The first case may occur for one or a series of closely related systems and is unlikely to have a general character. According to the present experience the second alternative is quite unlikely as well. The third alternative may lead to a wrong evaluation of the quality of some approximate computational schemes.[56]

According to the present discussion it is not surprising that our value of α is not precisely equal to the experimental result. In view of all approximations involved in its calculation it simply cannot be expected. If it were, we would have had to consider such an agreement as fortuitous. This is indicated by the magnitude of the correlation correction in the fourth-order treatment. Assuming, for instance, that the correlation perturbation series has a geometric character, the expected fifth-order correlation contribution to α should be of the order of -0.040 a.u., i.e., it will be at least non-negligible for achieving perfect agreement with experiment. A similar analysis can be carried out for other polarizabilities and makes one rather skeptical as regards the quality of theoretical data.

The above skepticism, however, does not make the approximate theoretical data useless. The higher-order polarizabilities are either inaccessible from the experimental data or difficult enough to measure that even approximate theoretical information is quite desirable. The results of the present paper show that in order to make this information reliable one has to consider carefully the electron-correlation contribution in the most complete and systematic way.

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