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Ab initio g-Hartree calculations on the atoms Be and Ne that employ fully numerical and basis-set techniques

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We report fully numerical calculations of correlation energies in second-order perturbation theory based on Hartree-Fock and g-Hartree mean fields for Be and Ne atoms and show that basis-set techniques give essentially the same results. An extension to higher-order perturbation theory is relatively straightforward in the basis-set approach. We report third-order calculations that yield in the case of Be significantly improved values for the g-Hartree correlation energy which now agrees within 4% with the total correlation energy known from complete configuration-interaction estimates, while third-order Hartree-Fock correlation energies calculated in the same basis set still disagree by 10% due to difficulties in describing the near degeneracy of the $2s$ and $2p$ orbitals. In the case of the Ne atom, we find that for the g-Hartree mean field still higher orders of perturbation theory are required to obtain agreement with experiment.

I. INTRODUCTION

The g-Hartree approach to electronic structure calculations on atoms and molecules has been introduced by Dietz, Lechtenfeld, and Weymans[1,2] as an alternative method for the modeling of correlations in interacting many-particle systems. In their first paper Dietz and his co-workers showed that the g-Hartree equation describes a mean field corresponding to the stationary point of the integrand in an integral representation of the generating functional for Green's functions of the fermion system under consideration.[1] Because of the stationary property, it was expected that perturbation expansions around the g-Hartree mean field should converge particularly fast. First results were encouraging,[2] but had to be restricted to second-order perturbation theory, which in turn was shown to yield good results in the case of ionization energies.[3] Total energies are, however, overestimated in second-order perturbation theory.[4,5] It has been conjectured[4] that the self-energy contributions, present in the mean-field energy and the first-order correction impede the fast convergence of the Møller-Plesset–type[6] perturbation series for g-Hartree mean fields. Practical calculations of the higher-order contributions, which could decide this question, were not done, however, and are, at present, not feasible using the fully numerical methods employed in Refs. 2 and 3. We propose using instead the basis-set methods developed in quantum chemistry,[7] which under certain circumstances allow for the calculation of perturbation contributions of very high order.[8]

In this paper we compare fully numerical calculations for the Be and Ne atoms with basis-set calculations in order to show that both methods yield essentially the same results. This may be surprising at first sight, since Møller-Plesset perturbation theory around Hartree-Fock orbitals exclusively encompasses integrals over continuum orbitals in the fully numerical calculations, whereas there are no continuum orbitals at all present in the basis-set calculations. Although powerful results are known about the convergence properties of variational approximations to bound states within discrete basis sets[9] and the convergence of expectation values,[10] the arguments in these papers are not applicable to matrix elements between a bound state and a continuum state, describing a virtual scattering event to model correlation contributions in the framework of many-body perturbation theory or one of its variants. Basis-set approaches to scattering theory are, however, discussed in a paper by Reinhardt.[11] In this instance, the basis-set method may be developed as a quadrature approximation to the spectral resolution of the Hamiltonian operator, interpreting appropriate quantities of the basis-set procedure as numerical quadrature abscissas and weights.

The plan of the paper is as follows: After a short review of the theory we discuss the technical details of the calculations and present the fully numerical and basis-set results for second-order Hartree-Fock–Møller-Plesset perturbation-theory calculations on the Be and Ne atom. We also include third-order results in the case of the basis-set calculations. Finally, we discuss the impact of these calculations on the question of convergence of the perturbation series.

II. THEORY

The g-Hartree orbitals $\{\psi_i(x)\}_{i\in I}$ are defined as the eigenvectors of the Fock matrix of g-Hartree theory:

TABLE I. Be-atom fully numerical calculations. HF and MP denote Hartree-Fock and Møller-Plesset schemes, respectively.

Maximum l	Second-order HF-MP correlation energy[a] (a.u.)	Nonrelativistic pair energy sums (Ref. 22)	$g_{\text{opt}}^{(2)}$	Second-order g-Hartree energy[b] (a.u.)
p	−0.0678	−0.0618	0.721 834	−0.0965
d	−0.0757	−0.0694	0.721 039	−0.1046
f	−0.0780	−0.0716	0.720 899	−0.1066

[a] The Dirac-Fock energy for the Be atom is −14.575 892 a.u.

[b] This energy was calculated using $g_{\text{opt}}^{(2)}$.

$$F_{ij}=h_{ij}+\sum_k n_k[gV_{ijkk}-(1-g)V_{ikjk}] , \tag{1}$$

with

$$h_{ij}=\int d\mathbf{x}\psi_i^*(\mathbf{x})[-\tfrac{1}{2}\Delta+V(x)]\psi_j(\mathbf{x}) , \tag{2}$$

$$V_{ijkl}=\int\int d\mathbf{x}\,d\mathbf{y}\psi_i^*(\mathbf{x})\psi_j(\mathbf{x})\frac{1}{|\mathbf{x}-\mathbf{y}|}\psi_k^*(\mathbf{y})\psi_l(\mathbf{y}) , \tag{3}$$

with $V(\mathbf{x})$ denoting the external (nuclear) potential and n_k the occupation number of orbital n_k. It can be shown[1] that for $g\in\mathbb{R}$ the g-Hartree mean field corresponds to a stationary point of the integrand in a functional integral representation of the partition function for a grand canonical ensemble, describing the interelectronic repulsions as a fluctuating external field. It should be noted that this representation, which is obtained by using the Hubbard-Stratonovich transformation,[12] contains no approximations. The g-Hartree mean field is the result of a saddle-point approximation to this integral. Dietz and Weymans[2] discussed the question of whether the real number g can be optimized in a certain sense, and they proposed an *ab initio* procedure that leads to the ground-state energy, exact to some specified order in perturbation theory, by requiring that the perturbation contributions be zero to that order

$$E=E_{g\text{-H}}+E_1+E_2+\cdots+E_n , \tag{4}$$

$$E_1+E_2+\cdots+E_n=0 , \tag{5}$$

whereby E_k denote the perturbation contributions in a Møller-Plesset–type[6] partition of the exact Hamiltonian operator H, treating $H-F$ as a perturbation with F denoting the Fock operator. $E_{g\text{-H}}$ is the g-Hartree mean-field energy in

$$E_{g\text{-H}}=\sum_i n_i h_{ii}+\tfrac{1}{2}\sum_{i,k} n_i n_k[gV_{iikk}-(1-g)V_{ikik}] . \tag{6}$$

The perturbation contributions may be written in terms of a Goldstone-type[13] diagrammatic expansion

$$E_1=\tfrac{1}{2}(1-g)\sum_{i,k} n_i n_k V_{iikk}-\tfrac{1}{2}g\sum_{i,k} n_i n_k V_{ikik} , \tag{7}$$

$$\begin{aligned}E_2&=I_1+I_2+I_3+I_4+I_5\\&=-\sum_{i,j,k,l}\left[n_i(1-n_j)n_k n_l\frac{1}{\varepsilon_j-\varepsilon_i}[(1-g)^2V_{ijkk}V_{ijll}-2g(1-g)V_{ijkk}V_{iljl}+g^2V_{ikjk}V_{iljl}]\right]\\&\quad-\tfrac{1}{2}\sum_{i,j,k,l}\left[n_i(1-n_j)n_k(1-n_l)\frac{1}{\varepsilon_j-\varepsilon_i+\varepsilon_l-\varepsilon_k}(V_{ijkl}V_{ijkl}-V_{ijkl}V_{ilkj})\right] .\end{aligned} \tag{8}$$

TABLE II. Be-atom nonrelativistic basis-set calculations.

Basis set	E_{HF} (a.u.)	Correlation energy (a.u.) Second-order HF-MP	Correlation energy (a.u.) Third-order HF-MP	$g_{\text{opt}}^{(2)}$	Second-order g-Hartree energy[a] (a.u.)	$g_{\text{opt}}^{(3)}$	Third-order g-Hartree energy[a] (a.u.)
$5s8p$	−14.572 526	−0.0619	−0.0763	0.721 818	−0.0964	0.722 751	−0.0869
$5s8p4d$	−14.572 588	−0.0699	−0.0821	0.720 846	−0.1065	0.722 616	−0.0885
$5s8p4d3f$	−14.572 588	−0.0714	−0.0834	0.720 666	−0.1083	0.722 509	−0.0896

[a] These energies are calculated using $g_{\text{opt}}^{(2)}$ and $g_{\text{opt}}^{(3)}$, as appropriate.

TABLE III. Be atom—contribution of individual diagrams. c and b denote continuum- and bound-state contributions, respectively. All values are given in a.u. for the nonrelativistic calculations.

	I_1	I_2	I_3	Sum[a]	I_4+I_5	p limit	d limit	f limit
c	−0.0138	0.3782	−1.2743	−0.0186	bb	−0.0465	−0.0466	−0.0466
b	−0.0303	0.1321	−0.6077	−0.0097	bc	−0.0094	−0.0100	−0.0100
sum	−0.1683	0.5103	−1.8820	−0.0283	cc	−0.0402	−0.0482	−0.0503
					sum	−0.0962	−0.1048	−0.1070
basis set	−0.1702	0.5197	−1.9276	−0.029		−0.0965	−0.1065	−0.1083

[a] Including g factors.

The ε_i denote the canonical orbital energies. In this paper, we optimize g to second and third order, i.e., we determine g, such that

$$E_1+E_2=0 \quad \text{for } g=g_{\text{opt}}^{(2)}\ , \tag{9}$$

$$E_1+E_2+E_3=0 \quad \text{for } g=g_{\text{opt}}^{(3)}\ . \tag{10}$$

We did not write down the Goldstone diagrammatic expansion for E_3, but rather determined E_3 from simple Rayleigh-Schrödinger theory. We also calculated perturbation expansions around the Hartree-Fock field using the appropriately modified expressions of Eq. (8). The one-particle graphs I_1-I_3 are, of course, equal to zero in this case.

III. TECHNICAL DETAILS OF THE CALCULATIONS

Fully numerical calculations were performed using a program developed for g-Hartree mean-field calculations by one of us,[14] based on the Dirac-Hartree-Fock (DHF) code by Johnson.[15] The program calculates bound states of the g-Hartree equation (also in its relativistic form) and the Dirac-Hartree-Fock equation, as well as continuum states, which are required to evaluate the perturbation sums of Eq. (8). QED corrections are calculated for the DHF case by means of Grant's program.[16] The basis-set calculations have been performed using newly developed programs for second- and third-order Møller-Plesset perturbation theory (evaluating also non-Hartree-Fock contributions) based on the standard HONDO Gaussian integral package.[17]

The basis set for the Be atom was derived from the (10s) basis set of Huzinaga using Dunning's contractions;[18] the p exponents were scaled from boron by a factor of 0.56 (Ref. 19). The resulting basis set (5s6p) was augmented by two functions with exponents 72.0 and 144.0 to the (5s8p) basis set used in the present calculations to span the s- and p-orbital angular momentum subspace. (Here the parentheses are used to represent the set of primitive Gaussians.) Two further basis sets were used to represent excitations in higher angular momentum subspaces, namely, a (5s8p4d) obtained from (5s8p) by addition of d functions with exponents 0.39, 1.6, 6.4, and 25.4; this one was in turn augmented to (5s8p4d3f) by f functions with exponents 32.0, 8.0, and 2.0. Since six component d functions and ten component f functions were used, the three basis set comprise 29, 53, and 83 contractions, respectively.

The neon atom basis set has been used by Klopper and Kutzelnigg[20] and derives from an (11s7p) basis set.[21] We use the (12s8p4d1f) uncontracted version and a (12s8p4d) set obtained by deleting the f function.

IV. RESULTS AND DISCUSSION

Results are collected for the Be atom in Tables I–III and for the Ne atom in Tables IV–VII. Table I gives second-order numerical Hartree-Fock–Møller-Plesset correlation energies and second-order g-Hartree energies for three calculations with different maximum values of the partial-wave angular momentum intermediate states. It should be noted that a fully numerical calculation also depends on a basis-set expansion (namely, a sum over infinitely many partial waves) with angular momentum l, which is only slowly converging. It is known[22–24] that

TABLE IV. Ne-atom fully numerical second-order Møller-Plesset correlation energies. The Dirac-Fock energy for the Ne atom is −128.6920 a.u. The corresponding nonrelativistic value is −128.5471 a.u.

	Correlation energy (a.u.)		
	This work		Ref. 25
Maximum l	Relativistic	Non-relativistic	Non-relativistic
p	−0.2067	−0.2063	−0.1920
d	−0.3413	−0.3409	−0.3224
f	−0.3654	−0.3650	−0.3603

TABLE V. Ne-atom fully numerical second-order g-Hartree calculations.

Maximum l	$g_{\text{opt}}^{(2)}$	Total g-Hartree energy (a.u.)	Second-order g-Hartree energy (a.u.)
d	0.841 024	−129.1127	0.4207
f	0.840 727	−129.1367	0.4447
d[a]	0.841 061	−128.9669	0.4198
f[a]	0.840 763	−128.9910	0.4439

[a] Nonrelativistic result.

TABLE VI. Ne-atom nonrelativistic basis-set calculations.

Basis set	E_{HF} (a.u.)	Second-order MP energy (a.u.)	Third-order MP energy (a.u.)	$g_{\mathrm{opt}}^{(2)}$	Second-order g-Hartree energy (a.u.)	$g_{\mathrm{opt}}^{(3)}$	Third-order g-Hartree energy (a.u.)
$12s8p4d$	−128.544 921	−0.3152	−0.3166	0.840 928	−0.4299	0.842 946	−0.2671
$12s8p4d1f$	−128.544 921	−0.3393	−0.3395	0.840 580	−0.4580	0.842 644	−0.2915

the partial-wave contributions vanish like $(l+1/2)^{-4}$, a result that may be traced to the singularity for coincident electron coordinates in the electronic repulsion operator. Klopper and Kutzelnigg[20] proposed a method of taking care of this "correlation cusp" by inclusion of appropriate functions into the basis set.

Our values compare well with previous work[22] estimating the angular momentum limits. Relativistic effects are negligible in the case of Be. For Ne (Table IV), relativistic contributions to the correlation energy are about 4×10^{-4} a.u. and thus of the order of our estimated accuracy of the numerical calculations. They also compare well and are actually slightly better than previous (basis-set) results.[25] We also give second-order Hartree-Fock–Møller-Plesset basis-set results (Tables II and VI), which are in good agreement with the numerical results.

The small difference is due to the finite basis-set representation of the r dependence within a partial wave, which leads to an underestimation of the second-order energies compared to the fully numerical results, which are converged within each angular momentum subspace. Second-order g-Hartree calculations exhibit similar convergence behavior with respect to the partial-wave expansion. Carrying the expansion to the f limit (Tables I and IV) shows that the second-order procedure overestimates correlation energies and thus higher orders in perturbation theory are required. The calculation of higher order is, however, much easier in a basis-set representation.

In order to evaluate the feasibility of the basis-set approach, we compare in detail the contributions to the second-order sum in terms of the diagrams written down in Eq. (8). The results are collected in Tables III and VII, and show good agreement of numerical and basis-set techniques. Note that the basis-set results include bound-state as well as continuum contributions. As a consequence, we propose to calculate higher orders using a basis-set approach, and present data for the third order in Tables II and VI. Table VIII provides a comparison with experimental estimates,[26] for which we assume uncertainties of one part in 10^{-4} for the contributions of successive ionization potentials, and thus errors in the total energy on the order of 10^{-4} a.u. in the case of Be and 10^{-3} a.u. in the case of Ne. We include also QED corrections and a quotation of configuration-interaction (CI) data for the correlation energy.[27,28] Note that the third-order energies derive from the largest nonrelativistic basis-set calculations reported in this paper, and that the CI results also derive from nonrelativistic calculations. The numbers show that for the Be atom the third-order g-Hartree theory is in good agreement with experiment and CI calculations, whereas convergence is still slow for the Ne case.

V. SUMMARY

Using basis-set methods, it is comparatively straightforward to calculate third-order energies, and we showed that third-order g-Hartree energies indeed give a better approximation to the total energy for the Be atom than Hartree-Fock (HF) third-order energies do, if our analysis relies on basis-set calculations. It should be noted that there is still a demand for fully numerical third-order calculations for benchmark purposes, since basis-set values of the third-order energies do not constitute an upper bound to the fully numerical third-order energies.

Needless to say, Be is a special case because of the near degeneracy of $2s$ and $2p$ orbitals, and the results for Ne (for which the second-order Hartree-Fock approximation is excellent) indicate that third-order perturbation theory may not be sufficient in the general case. Calculations up to 30th order of perturbation theory on the Be atom[29] show, however, that the g-Hartree perturbation series

TABLE VII. Ne atom—contribution of individual diagrams. c and b denote continuum- and bound-state contributions, respectively. All values are given in a.u. for the nonrelativistic calculations.

	I_1	I_2	I_3	Sum[a]	I_4+I_5	d limit	f limit
c	−0.6071	4.2496	−32.3371	−0.1086	bb	−0.0064	−0.0064
b	−0.2883	2.0672	−14.8980	−0.0269	bc	−0.0482	−0.0484
sum	−0.8954	6.3168	−47.2351	−0.1356	cc	−0.3159	−0.3393
					sum	−0.3706	−0.3940
Basis set	−0.9292	6.8472	−48.5103	−0.1404		−0.3753	−0.4028

[a] Including g factors.

TABLE VIII. Comparison of the fully numerical calculations with experiment (all energy values are given in a.u.).

	Configuration interaction	Second-order MP energy	Second-order g-Hartree energy	Third-order g-Hartree energy
		Be		
DHF	$-14.575\,892$	$-14.575\,892$	$-14.575\,892$	$-14.575\,892$
E_{corr}	-0.0934^{a}	-0.0780	-0.1066	-0.0896^{b}
QED corrections[c]	$0.000\,972$	$0.000\,972$	$0.000\,972$	$0.000\,972$
Sum	-14.6683	-14.6529	-14.6815	-14.6645
Experiment[d]	-14.6693			
		Ne		
DHF	-128.6920	-128.6920	-128.6920	-128.6920
E_{corr}	-0.385^{e}	-0.3654	-0.4447	-0.2915^{f}
QED corrections[c]	$0.002\,61$	$0.002\,61$	$0.002\,61$	$0.002\,61$
Sum	-129.0509	-129.0313	-129.1106	-128.9574
Experiment[d]	-129.0602			

[a] Nonrelativistic complete CI estimate (Ref. 27).

[b] Nonrelativistic basis-set calculation with $5s8p4d3f$ basis set.

[c] Evaluated from a DHF calculation using Grant's code (Ref. 16).

[d] Reference 26.

[e] Nonrelativistic complete CI estimate (Ref. 28).

[f] Nonrelativistic basis-set calculation with $12s8p4d1f$ basis set.

converges significantly faster than HF perturbation series, and we expect this to be the case whenever the correlations are so large that HF perturbation theory breaks down. For systems with more than four electrons we conjecture that higher than double substitutions become increasingly important in such cases, and thus convergence will be obtained only in fourth or higher order also in the g-Hartree case.

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