A NEW FUNCTIONAL FOR VARIATIONAL CALCULATION
OF ATOMIC AND MOLECULAR SECOND-ORDER CORRELATION ENERGIES

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Second-order correlation energies for atoms and molecules are calculated with a novel variational functional that is closely related to the one used before but neglects the most time-consuming terms. Consequently much larger basis sets could be used. Results for He, Be, H_2 and LiH obtained with an explicitly correlated gaussian geminal basis are better than the best published results by 0.32, 0.06, 3.3, and 6.2% and are estimated to be accurate to within a fraction of 1%.

Calculation of the correlation energy for atoms and molecules using many-body perturbation theory (MBPT) has been one of the most successful implementations of this theory [1]. There have always been two major areas of investigations: calculations of the most important components in higher orders of MBPT (see ref. [2] for a recent review) and calculations of low-order corrections, especially the second-order one, $E^{(2)}$, with increased accuracy (see e.g. refs. [3–11]). Due to the recent progress in the former field [2], the latter one, which reduces to solving the familiar basis set problem, seems to be more important at present. in a typical case presented in ref. [2] the $E^{(2)}$ error determines the accuracy of the final result. To improve the accuracy of $E^{(2)}$ the standard method of summation over a set of virtual orbitals is usually abandoned and the first-order pair equations are solved directly [3–11]. In this way second-order energies with accuracies higher than 99% have been obtained for the first-row closed-shell atoms [3–6, 9–11]. The numerical techniques employed in these calculations are hard to extend to molecules. An exception is a method used by Pan and King [6] which amounts to solving the pair equations variationally with a basis set of gaussian geminals that are explicitly correlated by a factor $\exp(-\gamma r_{12}^2)$ where r_{12} is the distance between the electrons 1 and 2. A modified version of this approach has been employed by Adamowicz and Sadlej [7,8] for the H_2, LiH, and BH molecules. The basis set of explicitly correlated gaussian functions has also proven to be capable of reproducing accurately correlation effects in a variety of observables like polarizabilities [12], Compton profiles [13], interatomic potentials [14] and generalized oscillator strengths [15].

If for a closed-shell system the zeroth-order problem is determined by a set of HF SCF equations

$$f\phi_\alpha = e_\alpha \phi_\alpha , \tag{1}$$

where f is the Fock operator, ϕ_α is the orbital and e_α is the orbital energy, then the first-order spin-free pair functions $\tau_{\alpha\beta}^i$ are defined by the equations

$$[f(1) + f(2) - e_\alpha - e_\beta]\tau_{\alpha\beta}^i(12) = -q_2 r_{12}^{-1} \varphi_{\alpha\beta}^i(12) , \tag{2a}$$

$$\tau_{\alpha\beta}^i = q_2 \tau_{\alpha\beta}^i , \tag{2b}$$

where $i = 1$ and 3 for singlet and triplet pairs, respectively, q_2 is the strong orthogonality projector,

$$q_2 = [1 - p(1)] [1 - p(2)] , \qquad p = \sum_\alpha |\phi_\alpha\rangle\langle\varphi_\alpha| , \qquad (3)$$

and $\phi^i_{\alpha\beta}(12) = \phi_\alpha(1)\phi_\beta(2) + (2 - i)\phi_\beta(1)\phi_\alpha(2)$. The pair functions can be calculated variationally by minimizing the functional

$$\epsilon^i_{\alpha\beta} \leqslant \mathcal{F}^i_{\alpha\beta}[\tilde{\tau}] = i(1 + \delta_{\alpha\beta})^{-1} [\tfrac{1}{2}\langle\tilde{\tau}|f(1) + f(2) - e_\alpha - e_\beta|q_2\tilde{\tau}\rangle + \langle\tilde{\tau}|q_2 r^{-1}_{12} \phi^i_{\alpha\beta}\rangle] , \qquad (4)$$

where $\tilde{\tau}$ is a trial function and $\epsilon^i_{\alpha\beta}$ are pair energies, the sum of which gives $E^{(2)}$. The above functional can be called the strong orthogonality functional.

Computer-time requirements are known to be a major limitation of Pan and King's approach since the method requires an extensive optimization of the non-linear parameters in the correlated gaussian geminals. The most time-consuming terms result from the presence of the fq_2 operator in eq. (4). The modification introduced by Adamowicz and Sadlej [7] further increases the time of a single calculation but allows the use of smaller orbital basis sets in the optimization stage.

It is possible, however, to replace the functional (4) by a simpler one which will be called the weak orthogonality functional,

$$\epsilon^i_{\alpha\beta} \leqslant \mathcal{G}^i_{\alpha\beta}[\tilde{\tau}] = i(1 + \delta_{\alpha\beta})^{-1} [\tfrac{1}{2}\langle\tilde{\tau}|f(1) + f(2) - e_\alpha - e_\beta + \Delta_{\alpha\beta}P(1) + \Delta_{\alpha\beta}P(2)|\tilde{\tau}\rangle + \langle\tilde{\tau}|q_2 r^{-1}_{12}\phi^i_{\alpha\beta}\rangle] , \qquad (5)$$

where $\Delta_{\alpha\beta}$ is an arbitrary real number greater than $\tfrac{1}{2}(e_\alpha + e_\beta - 2e_{LOMO})$ with e_{LOMO} denoting the lowest occupied molecular or atomic orbital. Asymptotically, for large geminal basis sets, this functional reduces the time of a single calculation by a factor equal to the square of the number of orbital basis functions. One can easily verify that functional (5) has the same minimal value as functional (4) and that the pair function minimizing functional (5) satisfies automatically condition (2b).

The $E^{(2)}$ energies presented in table 1 were obtained by expanding $\tilde{\tau}$ in terms of explicitly correlated gaussian geminals and carefully optimizing all linear and non-linear parameters. The present results improve the best published values of $E^{(2)}$ by 0.32, 0.06, 3.3 and 6.2% for He, Be, H_2, and LiH, respectively. For the Be atom our energy is negligibly lower than Lindgren and Salomonson's [10] "basis-set independent" result, thus confirming an accuracy of $\approx 10^{-5}$ au estimated by these authors, and showing again the quality of the basis set used in the present work. On the basis of the He and Be results the errors of our $E^{(2)}$ energies in the 20-geminal basis sets may be estimated to amount to a fraction of one percent.

In order to avoid here a discussion of the dependence of $E^{(2)}$ on the size of the orbital basis set, very accurate SCF orbitals composed of spherical gaussian functions (with floating centers for H_2 and LiH) have been used for the final calculation. Expansions half as long give $E^{(2)}$ within $\approx 10^{-5}$ au and expansions as short as four functions per orbital can be effectively used in the optimization stage.

Table 1
Second-order energies (in au)

	He	Be	H_2 $R = 1.4$	LiH $R = 3.015$
number of orbital basis functions	20 [16]	28 [16]	31	30
SCF energy	−2.86167995 [16]	−14.57302313 [16]	−1.1336287	−7.9873231
SCF "limit"	−2.86168000 [17]	−14.57302318 [16]	−1.133630 [18]	−7.987313 [19] −7.98734 [20]
number of geminal basis functions	40	40	20	20
$E^{(2)}$ present work	−0.037372	−0.076323	−0.034111	−0.071913
$E^{(2)}$ literature	−0.03725 [4]	−0.07628 [10]	−0.03303 [7]	−0.06773 [8]

Table 2
Comparison of total correlation energies

	He	H_2 $R = 1.4$	LiH $R = 3.015$
$E^{(2)}$	−0.03737	−0.03411	−0.07191
higher-order corrections	−0.00478 a)	−0.00605 b)	−0.01157 c)
total	−0.04215	−0.04016	−0.08348
"limit" correlation energy	−0.04204 d)	−0.04085 e)	−0.08317 f)
percent of the correlation energy	100.26	98.3	100.4
"best" previous MBPT result	−0.04203 [4]	−0.03908 [7]	−0.07696 [21]
percent of the correlation energy	99.98	95.7	92.5

a) Sum of third-, fourth-, and fifth-order corrections, from ref. [4].
b) Sinanoğlu's "exact pair" energy (which is equivalent to the linear CCM result) minus $E^{(2)}$ calculated in the same basis set, from ref. [7].
c) [2/1] Padé approximant minus $E^{(2)}$ calculated in the same basis set, from ref. [21].
d) Theoretical, refs. [17,22].   e) Theoretical, refs. [18,23].
f) Mixed experimental and theoretical, computed using data from refs. [20,24].

Work on higher-order corrections is in progress. However to show here the significance of accurate second-order energies for the final accuracy, our $E^{(2)}$ corrections are combined with published higher-order corrections and are compared in table 2 with some "limit" values of the correlation energy.

For the Be atom our result is essentially the same as that of Lindgren and Salomonson [10] and therefore has not been included in table 2. For the He atom our slightly better $E^{(2)}$ leads to a poorer agreement with the exact correlation energy, especially when taking into account that the corrections of sixth and higher order, neglected by Byron and Joachain [4], can be estimated with the geometric approximation to be equal to -4×10^{-5} au. This shows that the value of $E^{(3)} + E^{(4)} + E^{(5)}$ obtained by Byron and Joachain is still in error of ≈0.00015 au. This error is probably caused by the very slow convergence of the partial wave expansion for third-order energies observed recently by Jankowski et al. [25]. The very good agreement for LiH is probably accidental. It results from a cancellation of the basis set effect influencing the included higher-order corrections [21] with those MBPT contributions which were neglected [21].

In summary we have proposed and implemented a computationally more efficient functional to variationally obtain high-accuracy second-order energies. With the present approach we are able to match the "basis-set independent" results which are available for atoms and at the same time to obtain a similar accuracy for small molecules. The results reported here are for the diatomic molecules but our program also handles the polyatomic molecules. Work on this application is in progress.

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