

APPLICATION OF MP2 RESULTS IN COMPARATIVE STUDIES OF SEMIEMPIRICAL GROUND-STATE ENERGIES OF LARGE ATOMS

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To study the usefulness of second-order Møller–Plesset (MP2) correlation energies for ground states of closed-shell atoms (referred to as MP2/CA energies) in estimations of the total correlation energies of larger closed-shell atoms, we have considered atoms and ions containing from 10 to 86 electrons. First, it is demonstrated that for N -electron systems, $10 \leq N \leq 18$, the MP2/CA energies provide very good approximations to the very accurate estimates of atomic correlation energies by Chakravorty and Davidson. Next, for systems with $10 \leq N \leq 54$, comparisons are made with the semiempirical energies obtained when using the models by Chakravorty and Clementi as well as by Clementi and Corongiu. Finally, for atoms with $10 \leq N \leq 86$, the MP2/CA energies are employed for comparison with DFT energies recently obtained by Andrae *et al.* (*Int. J. Quantum Chem.* **2001**, *82*, 227). The MP2/CA results proved to provide reasonable estimates to the total correlation energies in all the cases considered.

Keywords: Semiempirical calculations; DFT; MP2; Correlation energies; Quantum chemistry; Quantum mechanics; Wave functions.

The problem of providing a reliable description of the electronic structure of atoms, molecules and solids has been in the center of interest since the early days of quantum mechanics. A diversity of techniques has been put forward both on the nonrelativistic and relativistic levels of the theory. For a long time methods based on the use of (approximate) wave functions have dominated in theory and applications. The most serious challenge for these methods, which we shall refer to as WFT (wave function theory), has been the proper description of electron correlation effects, which is equiva-

lent to proceeding to methods yielding results of higher accuracy than the one-electron schemes of the Hartree-Fock (HF) type. During the last two decades, we can witness the eruptive development of methods within an alternative approach to many-electron systems – the density function theory (DFT) – based on the fundamental work of Hohenberg and Kohn¹ and Kohn and Sham². These methods, built on the relatively simple concept of electron density distribution, have nowadays become the most frequently used tool in the electronic structure theory (for details and references, see, *e.g.*, refs^{3,4}). However, from the methodological point of view, an essential drawback of DFT is that the exact functional dependence of the energy on the density remains unknown even for the ground state.

An important role in the development of new many-electron methods of adequate accuracy both in the WFT and DFT approaches is played by comprehensive investigations aiming at the evaluations of their dependability. Due to the absence of mathematical tools helpful in this respect, truly meaningful reliability assessments must rely on comparisons with highly accurate or exact (for model systems) *ab initio* results, which is presently possible within the wave function approaches where there are no uncertainty problems caused by the lack of knowledge of the energy functional.

Ground-state energies of atomic systems have always played an important role in studies of the accuracy of various quantum-chemical methods, which is due to the fact that spherical symmetry and one-center character makes it possible to attain results of higher accuracy than for molecules of the same number of electrons. Presently, an important field of applications of these energies is investigations aiming at improving the reliability of DFT methods. These results are useful in several ways, for example, (i) for calibrating new functionals and providing reliability tests for the existing DFT models (*cf.* refs^{5,6}); (ii) in studies on improved DFT simulations of non-dynamical correlation effects (see, *e.g.*, refs^{7,8}); (iii) in studies of the influence of core-valence separation on the structure of electron densities (*cf.* ref.⁹).

Applications of the type just mentioned are severely limited by the lack of WFT information on the structure of electron correlation effects in larger atoms, *i.e.*, for systems for which the DFT models are most readily applied. In the present investigations we are concerned with various nonrelativistic methods of calculating the energy of closed-shell atoms including up to 86 electrons. We realize that for larger atoms comparison of these results with experimental energies would require taking into account very significant relativistic effects. However, the knowledge of correlation energies for large atoms is important from the methodological point of view. This knowledge

is helpful in setting up semiempirical models for treating correlation effects within the WFT as well as in studying the usefulness and the applicability range of various approximate DFT functionals. In fact, large atoms are very attractive in this respect as in their inner- and outer-most regions the electrons move in different close-to-extreme conditions.

To better motivate the main aim of the present work, we will start with a quick look at the atomic correlation problem within the framework of the wave function approach.

RESULTS AND DISCUSSION

Present State of Information on Correlation Energies for Larger Atoms

Results of very high (spectroscopic) accuracy are presently available only for very small atomic systems including just two, three or four electrons (see, *e.g.*, ref.¹⁰). For example, the accuracy of available variational energies, which provide upper bounds to the exact energies, drops rapidly as the number of electrons in the atom increases. For 10-electron atoms (Ne) the variational result represents about 97.7% of the exact correlation energy, E_{corr}^{11} ($E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}^{12}$). For 12-electron systems (Mg), the variational result amounts only to 93.3%¹³. Finally, for 18-electron atoms so far one has obtained by variational methods only 90.9% of the exact correlation energies. For systems containing up to 12 electrons, there are several non-variational calculations which yield results of higher accuracy than their variational counterparts (see, *e.g.*, the results by Müller *et al.*¹⁴ and Gdanitz¹⁵, who obtained for Ne about 99.7% of the correlation energy). A consequence of the numerical demands of post-Hartree-Fock calculations is that for atomic systems containing more than 18 electrons, there are very few *ab initio* results for the correlation energies. As a rule, their accuracy is rather low, which is caused by the necessity of restricting the size of the basis sets (*e.g.*, by strongly restricting the *l*-values of atomic orbitals) as well as the number of correlated electrons (*e.g.*, to subsets of valence electrons).

Another source of atomic correlation energies is experimental (atomic spectroscopy) results corrected for relativistic effects. Work along these lines was initiated in the sixties (see, *e.g.*, refs^{16,17}) and continued up to the late eighties¹⁸. More recently, to improve the accuracy of previous results, Davidson, Hagstrom, Froese Fischer, Chakravorty *et al.*^{5,19,20}, by combining experimental data (sums of successive ionization potentials) and improved *ab initio* calculations of relativistic effects, have put forward a modified method of accurate estimation of ground-state correlation energies. Their

studies included atoms and ions with 3 to 18 electrons and nuclear charges up to $Z = 28$. We shall refer to these results as “accurate estimates of the nonrelativistic correlation energies” and denote them by $E_{\text{corr}}^{\text{estim}}$. It should be mentioned, however, that applying this approach to larger atoms seems to be an extremely difficult task, which would require intensive experimental work to provide the necessary spectroscopic data as well as new methods for estimating accurately the relativistic effects. This is a gloomy outlook from the general methodological point of view because the lack of trustworthy correlation energies for large atoms restricts the usefulness of WFT results in the search for universal physically motivated DFT functionals.

Taking into account the restricted possibilities in obtaining accurate *empirical* correlation energies for larger atoms, one should appreciate the efforts in setting up methods of estimating these energies based on sound model considerations. Let us just mention the two models representing extensions of the HF method. Both of them have been conceived for the treatment of atomic correlation effects but have been later generalized to molecular systems. The first of these approaches devised by Chakravorty and Clementi²¹ may be considered equivalent to employing perturbed Roothaan HF orbitals. It requires the re-evaluation of the two-electron integrals due to the introduction of a modified inter-electronic interaction potential, associated with a *soft Coulomb hole* whose magnitude is determined by a set of semiempirical parameters. The other model has been recently put forward by Clementi and Corongiu²² who have developed a different semiempirical approach to obtain the electron correlation energy. In this method one selects an effective Hamiltonian with small perturbations proportional to a function of electron density for the HF matrix elements. This function is represented by a set of parameters determined from experimental data. Whenever comparison is possible, the correlation energies obtained are reasonably close to the accurate estimates by Chakravorty and Davidson.

In closing this quick look at the atomic correlation energy problem in WFT, we arrive at the rather pessimistic conclusion that for larger than 18-electron atoms we do not have access either to accurate *ab initio* results or to dependable estimates from experimental data. In addition, when proceeding to the largest atoms, the two semiempirical model approaches considered yield values that show increasing discrepancies with the empirical estimates by Chakravorty and Davidson.

The question arises: Is there a way to alleviate the problem of correlation energies for large atoms? We think, that to a certain extent, it is. We would suggest that rather than attempting to use advanced but prohibitively ex-

pensive *ab initio* methods to arbitrary large atoms, it might be better to apply an incomparably cheaper *ab initio* method to a properly chosen subset of atomic systems. In a recent review on the second-order picture of correlation effects in closed-shell atoms, the present authors²³ have presented arguments that for this important class of many-electron systems, second-order energies obtained within the framework of the Møller–Plesset perturbation theory (MP2)²⁴ based on the restricted-HF (RHF) zero-order problem may provide a source of reliable information concerning the correlation energy of larger atoms. This situation is due to two facts: First, for closed-shell atomic systems one has to deal with predominantly *dynamical correlation effects*²⁵ which are expected to be well represented by the lowest order of MP perturbation theory. Second, owing to the spherical symmetry of atomic systems, the MP2 energies can be calculated with extremely high accuracy if advantage is taken of the possibility of a systematic reduction of the problem into separate radial and angular subproblems. The radial part of the wave functions required in the calculations may be accurately represented either in terms of global or local basis sets. In the former case extensive sets of properly optimized Slater orbitals have been used (see, e.g., ref.²⁶), whereas in the latter case the *p*-version finite element formalism²⁷ is used. Accurate representations of the radial parts of the wave functions have been used in calculations of energy increments corresponding to all virtual orbitals, including those of very high angular momentum (up to $l_{\max} = 9$ or $l_{\max} = 12$). The remaining small portion of the second-order energy is obtained by angular extrapolation procedures based on mathematical considerations²⁸.

For closed-shell systems, in addition to their high accuracy, the various types of increments to the MP2 energies disclose interesting properties, which are very helpful for the rationalization of the structure of correlation energies even in nonclosed-shell atoms (for details see ref.²³).

Taking into account that most of the techniques used to attain the high accuracy of the MP2 energies are uniquely defined only for closed-shell atoms and that only for such atoms the increments to the MP2 energy disclose various interesting regularities, we refer to all such applications of the Møller–Plesset method by the acronym MP2/CA. Mention should be made that the use of extensive radial basis sets even in calculations of energy increments defined by orbitals corresponding to high *l*-values provides solid foundations for reliable extrapolating, which cause that the MP2/CA energies may be considered as practically basis-set-independent. Further justifications of such a characteristic is provided by extensive calculations of the

MP2/CA energies performed within four different realizations of the methodology sketched above (for details see ref.²³).

To demonstrate the accuracy of the MP2/CA correlation energies, we compare them in Table I with the latest accurate estimates, $E_{\text{corr}}^{\text{estim}}$ by Chakravorty and Davidson²⁰. Let us mention that a comparison of the MP2/CA values with the first accurate estimates by Davidson and coworkers¹⁹ has already been reported by one of us²⁹. One sees from the table that for all Z values considered, the agreement is higher than 95%. It is especially satisfactory for the Ne-like atoms, which is a consequence of the perfectly closed-shell structure of these systems. The degree of agreement reaches its low for the Mg-like ions at the highest value of Z considered ($Z = 28$), which is certainly a demonstration of quasidegeneracy effects for the $3s^2$ pair. Quasidegeneracy seems to have a smaller impact on the results for the Ar-like systems, for which one can even observe an improved agreement in the high- Z regime.

The high accuracy of the MP2/CA correlation energies for the ground states of atoms including up to 18 electrons may provide a justification of the expectation that also for larger closed-shell atoms the MP2/CA energies yield the bulk of the correlation energies. It is very unlikely that in the foreseeable future such portions of the correlation energies can be obtained by any of the more advanced *ab initio* methods. Our high accuracy expectations are further supported by the regularities disclosed by various contributions to these energies for varying N and Z values (for an extensive discussion, see ref.²³). An important argument for using MP2/CA energies

TABLE I
Comparison of accurate estimates of the correlation energies $E_{\text{corr}}^{\text{estim}}$ and MP2/CA energies (in E_h , all signs reversed)

Z	Ne-like		Mg-like		Ar-like	
	$E_{\text{corr}}^{\text{estim}}$ ^a	MP2/CA ^b	$E_{\text{corr}}^{\text{estim}}$ ^a	MP2/CA ^b	$E_{\text{corr}}^{\text{estim}}$ ^a	MP2/CA ^b
10	0.39120	99.21				
12	0.39060	98.93	0.43943	97.38		
18	0.39968	99.40	0.49648	97.01	0.72610	97.71
20	0.40205	99.54	0.50978	96.80	0.76174	97.97
28	0.40811	99.84	0.55363	95.78	0.87146	98.38

^a Chakravorty and Davidson²⁰. ^b % of $E_{\text{corr}}^{\text{estim}}$.

in correlation energy studies is the fact that they disclose the following important, but as yet “empirical”, property of second-order Møller–Plesset energies for closed-shell ground states: these energies are of smaller magnitude than the exact correlation energies. Hence, the sum of the accurate HF and MP2/CA energies provide upper bounds to the ground state energies.

The aim of this article is to test the usefulness of the MP2/CA approach in calculations of the total correlation energies of larger atoms. We present a compilation of published and unpublished MP2/CA energies for atoms and ions including from 10 to 86 electrons. Detailed information about the methods of calculation and extrapolation as well as references to already published energies are given in ref.²³ Energies for atoms containing up to 54 electrons are compared with their counterparts obtained when using the *soft Coulomb-hole* model of Chakravorty and Clementi²¹ and the model by Clementi and Corongiu²² based on the *virial constrained effective Hamiltonian*. Next we compare the HF plus MP2/CA energies for atoms and ions including up to 86 electrons with the DFT energies recently obtained by Andrae *et al.*³⁰

Comparison of MP2/CA and Semiempirical Correlation Energies

Table II collects the MP2/CA correlation energies for closed-shell atomic systems containing up to 54 electrons as well as the results obtained when using the semiempirical model approaches by Chakravorty and Clementi²¹ and Clementi and Corongiu²² mentioned above. To better appreciate the accuracies of the energies just mentioned, we have also included in the table the relevant $E_{\text{corr}}^{\text{estim}}$ results by Chakravorty and Davidson²⁰. We should underline that the semiempirical models considered are defined within the framework of WFT.

Let us start with the comparison of the MP2/CA correlation energies with their counterparts calculated when using the *soft Coulomb-hole* semiempirical model²¹. We shall refer to this model as *SCH model*. One can see from the table that, except for the Ne atom, the magnitudes of the SCH-model correlation energies are larger than of the MP2/CA ones. For systems containing up to 30 electrons, the differences are of the order of 5%. However starting with $N = 36$, one can observe a significant increase in these differences. For the largest atom (Xe), the MP2/CA energy amounts only to 77.0% of the SCH value! We do not find any explanation for this sudden increase in the disagreement between the results of the MP2/CA and SCH methods. Indications of the tendency of the latter method to overestimate the correlation energies can already be noted for such relatively small at-

oms like Mg and Ar for which the magnitudes of the SCH energies exceed the $E_{\text{corr}}^{\text{estim}}$ ones by about 1%. On the other hand, one can see in Table II that for Ne the magnitude of the MP2/CA energy discloses an unexpected behavior: it exceeds the SCH one by 11.8%. Proceeding to comparison of the MP2/CA energies with the results of the semiempirical model based on the virial constrained effective Hamiltonian²² (which we shall refer to as the VCEH model), one can see from Table II that for all but the Zn atom the magnitudes of the latter ones are larger by 4–10%. For Zn the magnitude of the MP2/CA energy is larger by 0.7% from the VCEH result. We note from the results for members of the Mg and Ar isoelectronic series that the agreement between the MP2/CA and VCEH energies improves with increasing nuclear charge. This tendency is not observed for the Ne series, where the differences are close to constant. It is apparent from the table that in all

TABLE II
Comparison of MP2/CA energies with “experimental” and semiempirical correlation energies (in E_h , all signs reversed)

Atom	N	MP2/CA ^a	Chakravorty and Davidson ^b	Chakravorty and Clementi ^c	Clementi and Corongiu ^d
Ne	10	0.38811	0.39120	0.347	0.4080
Na ⁺	10	0.38577	0.38978		0.4016
Mg ²⁺	10	0.38643	0.39210		0.4037
Mg	12	0.42793	0.43943	0.442	0.4656
Al ⁺	12	0.44022	0.45253		0.4645
Si ²⁺	12	0.44981	0.46337		0.4702
Ar	18	0.70945	0.72610	0.736	0.7817
K ⁺	18	0.72850	0.74452		0.7822
Ca ²⁺	18	0.74629	0.76174		0.7869
Ca	20	0.79816		0.843	0.8524
Zn	30	1.69746		1.740	1.6860
Kr	36	1.8907		2.262	2.0671
Sr	38	1.9772		2.436	2.1585
Cd	48	2.7253		3.453	3.0042
Xe	54	3.0877		4.010	3.4275

^a References to published results are given by Flores *et al.*²³ ^b Accurate estimates from experimental data²⁰. ^c “Soft” Coulomb-hole approach²¹; results published in ref.³² ^d Virial constrained effective Hamiltonian method²².

cases when comparison with $E_{\text{corr}}^{\text{estim}}$ is possible, the VCEH approach overestimates by 1.5–7% the accurate estimates of the correlation energy. For neutral atoms this overestimation increases with increasing number of electrons, which might be an indication of the fact that also for the largest atoms included in the table, the magnitudes of the VCEH energies are larger than the magnitudes of the accurate correlation energies.

In closing this discussion let us concentrate on comparison of the SCH and VCEH energies given in Table II. As may be seen in the table, up to $N = 20$, the magnitudes of the latter energies are larger than the former ones. For the $N \geq 30$, we deal with the reverse situation. The difference is especially pronounced for the largest atoms, e.g., for Xe it amounts to 17%. Since for this atom also the SCH energies are larger than the MP2/CA ones by about 30%, it is very likely that for larger atoms the SCH model provides a less accurate description of the correlation effects than the VCEH model. The present discussion does not lead to any conclusions concerning the relative accuracies of the MP2/CA and VCEH methods. The present VCEH results do not challenge our earlier statement that the MP2/CA energies are of smaller magnitudes than the exact correlation energies. It seems also very likely in most cases the magnitudes of the VCEH energies are larger than the magnitudes of the exact correlation energies.

Comparison with DFT Results for Larger Atoms

Very recently, to provide reference data for algebraic approaches and to compare various density functionals, Andrae *et al.*³⁰ have studied several density functionals in numerical, *i.e.*, basis-set-free, nonrelativistic Kohn–Sham² calculations for closed-shell atomic systems including up to 120 electrons. When discussing the accuracies of total energies obtained from calculations with various exchange-correlation energy density functionals, the authors mention the fact that exact nonrelativistic total energies for reliable comparisons are available only for the lightest atoms and, consequently, make such comparisons only for systems including up to 10 electrons. In the light of the arguments presented above, it seems that for a reasonable discussion of the accuracy of the remaining DFT results for the closed-shell atoms considered, it might be sufficient to use estimates of the total energy represented by the HF+MP2/CA *ab initio* energies.

Out of the three sets of results published by Andrae *et al.*³⁰, we have chosen for discussion two sets that yield the most accurate results, *viz.*, the results obtained for the exchange-correlation potentials LDA-VWN80³³ and van Leeuwen–Baerends³⁴ (LB94). The DFT energies along with the estimates

of the total nonrelativistic energies, $E_{\text{tot}}^{\text{nrrel}}$, are collected in Table III. Whenever possible, *i.e.*, for $N \leq 18$, we have used the formula

$$E_{\text{tot}}^{\text{nrrel}} = E_{\text{HF}} + E_{\text{corr}}^{\text{estim}}, \quad (1)$$

where $E_{\text{corr}}^{\text{estim}}$ results are taken from ref.²⁰ In the remaining cases the formula

$$E_{\text{tot}}^{\text{nrrel}} = E_{\text{HF}} + E_{\text{corr}}^{\text{MP2/CA}} \quad (2)$$

TABLE III
Energy differences, ΔE^{DFT} , between DFT and estimated nonrelativistic total energies, $E_{\text{tot}}^{\text{nrrel}}$ ^a (in E_{h})

Atom	N	ΔE^{DFT}		$E_{\text{tot}}^{\text{nrrel}}$ ^a
		LDA/VWN80 ^b	LB94 ^c	
Ne	10	0.70743	0.36105	-128.938298
Na ⁺	10	0.82048	0.38179	-162.066742
Mg ²⁺	10	0.93667	0.40054	-199.222910
Mg	12	0.91730	0.44184	-200.054066
Al ⁺	12	1.03085	0.45830	-242.127201
Si ²⁺	12	1.14672	0.47199	-288.459267
Ar	18	1.60467	0.76503	-527.543613
K ⁺	18	1.73152	0.78874	-599.762099
Ca ²⁺	18	1.85761	0.80694	-676.916093
Zn	30	2.9928	1.4746	-1779.5456
Kr	36	3.8255	1.8878	-2753.9457
Xe	54	6.4193	3.1609	-7235.2261
Ba	56	6.7027	3.2626	-7886.7643
Yb	70	8.5680	4.2931	-13396.5412
Hg	80	10.2603	5.2703	-18414.4425
Rn	86	11.2990	5.8089	-21872.5462

^a See the text, Eqs (1) and (2). ^b Vosko-Wilk-Nusair³³. ^c van Leeuwen-Baerends potential³⁴.

is employed. The values of $E_{\text{corr}}^{\text{MP2/CA}}$ for $N \leq 54$ are given in Table II. The MP2/CA correlation energies for Ba, Yb, Hg, and Rn amount to -3.2205 , -5.085 , -5.451 , and 5.774 hartree, respectively (see refs^{35,36}). From the results given in Table I, it is evident that using Eq. (2) instead of Eq. (1) would have no impact on our discussion.

As may be seen in Table III for all the atoms considered, the DFT total energies are higher than the estimated nonrelativistic total energies. The deviations with respect to the $E_{\text{tot}}^{\text{mrel}}$ values are almost twice larger for the calculations based on the VWN80 potential than for the LB94 one. Moreover, for neutral atoms, these deviations increase in a monotonic way when increasing the number of electrons. Let us notice that for the LB94 results the deviations are close to the magnitudes of the correlation energies and that in several cases these results are less accurate than their HF counterparts. For the VWN80 potential all the energies obtained are higher than their HF counterparts. The differences increase from the value of 0.3162 hartree for Ne to the value of 5.525 hartree for Rn. It seems that, the exchange correlation potentials considered by Andrae *et al.*³⁰ are not sufficiently well adapted for applications involving large atoms. Concluding, let us just mention, that the use in the estimates of the nonrelativistic total energies of semiempirical VCEH correlation energies discussed in the previous section would further deteriorate the agreement with the DFT results.

CONCLUSIONS

In a quick look at the present state of the electron correlation problem for larger atoms, we have indicated the lack of reliable results for these systems within the framework of the wave function theory (WFT). This situation has several negative consequences, *e.g.*, it limits the possibilities of using WFT energies for scaling DFT functionals in a very important range of applications. One way of alleviating this problem is the use of MP2/CA correlation energies for estimation of the values of the total correlation energies in large closed-shell atoms (see the discussion by Flores *et al.*²³). In this work we have studied the usefulness of the MP2/CA energies in estimations of the total correlation energies of larger closed-shell atoms. We have considered atoms and ions containing from 10 to 86 electrons. First, we have shown that for up to 18-electron systems, the MP2/CA energies provide very good approximations to the very accurate estimates of atomic correlation energies by Chakravorty and Davidson²⁰. Next, for N -electron systems with $10 \leq N \leq 54$, comparisons are made with the semiempirical energies obtained when using the WFT models by Chakravorty and Clementi²¹ as

well as by Clementi and Corongiu²². Finally, for atoms with $10 \leq N \leq 86$, the MP2/CA energies are employed for comparison with DFT energies very recently obtained by Andrae *et al.*³⁰ Let us mention, that within the framework of WFT, for systems with $56 \leq N \leq 86$, there are no other *ab initio* or semiempirical correlation energies available for comparison.

We have found that in all the cases mentioned, the MP2/CA results proved to provide reasonable estimates to the total correlation energies and have been useful in discussing the quality of semiempirical and DFT results.

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