
**STUDY OF POTENTIAL CURVES BY UHF-TYPE METHODS.
LINEARIZED COUPLED CLUSTER METHODS
WITH DOUBLE SUBSTITUTION**

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The potential energy curves have been calculated for LiH, Li₂, and N₂ molecules by means of the L-CCD method (Linearized Coupled Cluster Method with Double Substitutions) based on the UHF and RHF reference functions. With each of the molecules, peculiarities are discussed of the description of the curves by the UHF-type methods on the basis of comparison with the full CI or experimental curves. The L-CCD(UHF) method gives a qualitatively correct course within the whole range of internuclear distances.

In order to obtain a quantitative agreement with experimental data in the calculations of the potential energy hypersurfaces needed for determination of rate constants of chemical reactions, it is necessary to describe — as accurately as possible — the changes in electronic correlation energies of the reacting molecular systems. Therefore, very exact methods of quantum chemistry must be chosen to obtain the chemical accuracy, but they are so exacting with respect to numerical calculations that their application to greater molecules is impossible. In the search for a compromise, a suitable intermediate step can be found in the linearized coupled cluster method with double substitutions (L-CCD) introduced into the quantum chemistry by Čížek¹. This method is based on the cluster expansion of reference Slater determinant, on approximative solution of the Schrödinger equation on the basis of projection into the subspace of the ground and the biexcited configurations, and on iterative solution of a system of linear equations resulting from neglectation of the quadratic terms. As this non-variation approach is closely related to other methods of inclusion of the electronic correlation effects, this method is also known under the abbreviation D-MBPT(∞) (ref.^{2,3}), CEPAO (ref.⁴⁻⁶), or that coined by the original authors L-CPMET (ref.^{1,7-9}). Detailed information on properties of the method and its relation to other theories of electronic correlation can be found in refs¹⁰⁻¹⁷. The present paper will only stress some of the advantages of the L-CCD method with regard to its application to construction of the potential energy hypersurfaces. First of all, it is known that the L-CCD method provides absolute values of the correlation energy which are relatively close to those obtained by the full CI method. For illustration: the H₂O molecule has the full CI correlation energy of 388.6 kJ/mol in the double zeta basis set¹⁸, whereas the L-CCD method gives 382.3 kJ/mol in the given basis set. High efficiency of this non-variation method is explained by convenient error cancelation^{13,17}. The analysis¹⁹ shows that the compensation is not only incidental, but the values close to the full CI values are physically justified. According to this analysis, the CCD methods are characterized by an enhancement of the weighting of double substitutions which correctly reflects the involvement of the higher-level substitutions into the CI wave function. Another advantage of the L-CCD

method consists in the fact that it (as one of only few non-variation methods) enables a simplification of calculation of the analytical energy gradient²⁰ necessary in the optimizing procedures for finding the minima and saddle points on a potential energy hypersurface. This useful property follows from the fact that the L-CCD correlation energy can be considered as the minimum of the third-order Moller-Plesset perturbation expression with respect to the CI coefficients²⁰.

One of the most important properties of the methods of calculation of electronic correlation energy is their size consistency²¹. Only the size-consistent methods ensure a continuous approach to the dissociation limits in the description of potential energy hypersurfaces. In this context it must be stressed that not only the way of inclusion of the correlation effects but also the reference function are decisive for the resulting method to be size consistent. So *e.g.* the single RHF Slater determinant only gives a size-consistent wave function, if it is combined with full CI. The MC SCF reference function which is size consistent at a suitable choice of the Slater determinants can be combined with the size-consistent CC or with the perturbation methods of calculation of the correlation energy^{15,22,23}. So far, however, such combination of methods involves many problems which prevent its current practical applications. The UHF reference function which is size consistent and combined with the size-consistent L-CCD method seems to be a suitable compromise in this situation. This combination of methods includes the above-mentioned advantages of the L-CCD method but also the problem of the spin contamination of UHF determinant which causes deformation of the potential curves in the region of medium internuclear distances. The aim of this communication is to show the extent to which the L-CCD method can remove this drawback of the UHF reference function.

Potential Curves of LiH, Li₂ and N₂ Molecules

The said molecules represent — with respect to non-stability of the RHF wave function — the following three situations. The LiH molecule as well as most stable closed-shell molecules have a stable RHF solution in the region of equilibrium geometry, and a different UHF solution begins to appear only in the region of $R > R_c$. On the other hand, the Li₂ molecule has its non-stability threshold at $R < R_c$, which means that there exists a non-trivial UHF solution in the equilibrium region. The N₂ molecule has the non-stability threshold near R_c . This effect deforms the UHF potential curves in different ways in these three cases.

First of all our attention will be focused on the dissociation energies. Their values calculated in our standard combination of the minimum basis set + bond functions centered in the middle of bond²⁴ (this basis set is used throughout in this communication) are presented in Table I. The results show that the L-CCD(UHF) method does not substantially change the dissociation energies as compared with the second-order perturbation theory (the abbreviation L-CCD(UHF) means that the UHF determinant was used as the reference function).

The overall shape of the L-CCD potential curves of LiH molecule is compared in Fig. 1 with the curves obtained by RHF, UHF, UMP2, and full CI methods²⁴. The best agreement with the full CI in the given basis is shown by the L-CCD(RHF) curve which, however, ceases to be correct from the distances of about 0.3 nm, the L-CCD expansion being divergent at higher distances. The L-CCD(UHF) method, which – compared with the full CI – improves the drawbacks of the UHF reference function to considerable extent, shows deviations in the region of medium distances. These deviations are somewhat lower than those of the UMP2 method.

TABLE I

Dissociation energies of LiH, Li₂ and N₂ molecules in kJ/mol

Molecule	UMP2	UMP3	L-CCD(UHF)	Exp
LiH	237	250	256	243
Li ₂	49	55	62	103
N ₂	734	698	724	956

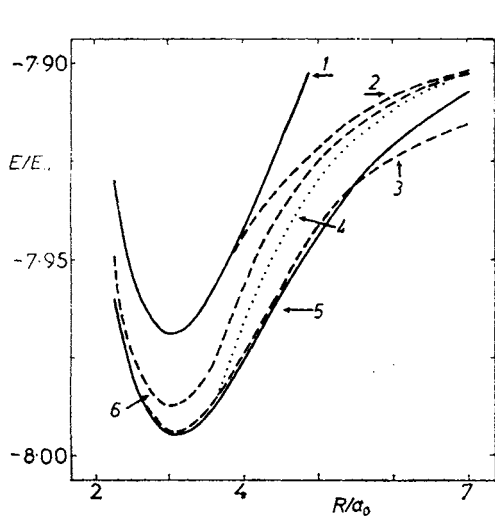


FIG. 1

Potential curves of the LiH molecule 1 RHF; 2 UHF; 3 L-CCD(RHF); 4 L-CCD(UHF); 5 full CI; 6 UMP2.

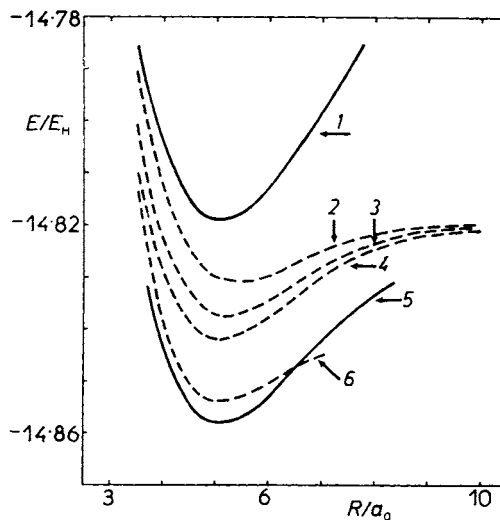


FIG. 2

Potential curves of the Li₂ molecule 1 RHF; 2 UHF; 3 UMP2; 4 L-CCD(UHF); 5 exp.; 6 L-CCD(RHF)

A slightly different character is seen in the curves of the Li_2 molecule in Fig. 2. The overall shape of the curves obtained by the individual methods is compared with the potential curve determined experimentally²⁵, this curve being shifted to have the same dissociation limit as the UHF-type curves. In this case the L-CCD.(RHF) method can describe a considerably smaller part of the equilibrium region. The L-CCD(UHF) curve has qualitatively the best shape. As the non-stability threshold of the RHF wave function is shifted deep into the repulsion part of the curves, the insufficient removal of spin contamination components of UHF wave function with L-CCD inclusion of the correlation effects will make itself felt just in the equilibrium region and will result in a small value of the dissociation energy.

A size-consistent and, at the same time, qualitatively correct description of dissociation of the N_2 molecule represents a hard problem for the quantum chemical methods. Fig. 3 shows the calculated potential curves in comparison with the curve obtained on the basis of experimental data²⁶. Again the L-CCD(RHF) method fails qualitatively at relatively low internuclear distances already. The UMP2 and specially the L-CCD(UHF) methods considerably improve the incorrect shape of the UHF reference function. It is interesting that in the equilibrium region the UMP2 curve lies below the L-CCD(UHF), which is due to a considerably great positive contribution of the 3rd order of the perturbation expansion of the L-CCD(UHF) energy. Properties of the L-CCD(UHF) curve show a certain discrepancy as compared with the results by Bartlett and Purvis³. These authors, using the basis¹³ ($4s\ 3p\ 1d$), obtained – near the equilibrium distance of the N_2 nuclei – a reverse curvature of the curve calculated on the basis of the UHF reference function. This

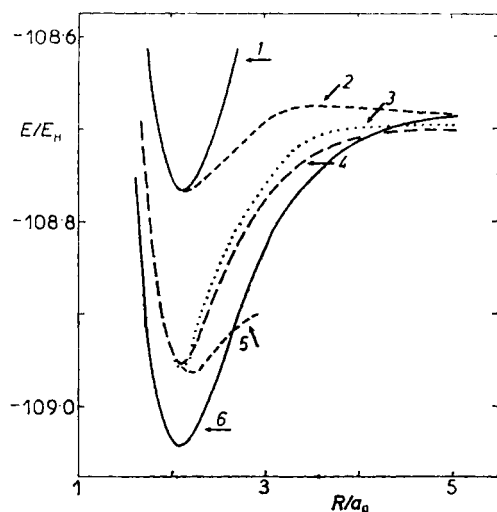


FIG. 3
Potential curves of the N_2 molecule 1 RHF; 2 UHF; 3 UMP2; 4 L-CCD(UHF); 5 L-CCD(RHF); 6 exp

fault appears on our UMP2 curve, but the inclusion of the contributions of the biexcited configurations up to the infinite order (which gives the L-CCD(UHF) energy) imparts to the curve a qualitatively correct course. This discrepancy is mainly due to the different character of our minimum basis with the bond functions as compared with the ($4a\ 3p\ 1d$) basis. Partially it is also due to the fact that Bartlett and Purvis³ finished the perturbation expansion of the L-CCD(UHF) function at the 6th order. According to our experience, the convergency of the perturbation expansion is very slow just in the region of medium internuclear distances, and neglect of higher orders can affect the overall shape of the curve.

CONCLUSIONS

The examples of the potential curves of the LiH, Li₂, and N₂ molecules showed that the L-CCD method of inclusion of the correlation electronic effects based on the UHF reference function can represent (if the basis set is chosen carefully) a very efficient method for description of the potential energy hypersurfaces. With relatively low demands for machine time this method is able to give a qualitatively correct course of the potential curves within the whole range of the internuclear distances. The deviations in the region of medium distances are due to imperfect removal of the spin contamination components of UHF reference determinant. For an improvement of the course in this region of distances it would be necessary to use the spin-adapted coupled cluster theory (*e.g.* that of the type used in ref.²⁷), whereby, however, simplicity of the method discussed would be lost.

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