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Dynamic correlation for MCSCF wave functions: An effective potential method

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A method is suggested which allows the inclusion of dynamic correlation into CASSCF calculations. An effective Coulomb hole potential is added to the Hamiltonian. The potential has a simple form, which allows its implementation into existing LCAO programs using Gaussian integral packages. The parameters appearing in the potential are determined by fitting to empirical valence correlation energies for first row atoms. Calculations of ionization energies and electron affinities show considerable improvement compared to the MCSCF values. Test calculations on three molecules give the following results, H_2: $r_e = 0.745$ (0.741) Å, $D_e = 4.62$ (4.75) eV; N_2: $r_e = 1.099$ (1.098) Å, $D_e = 10.42$ (9.91) eV; O_2: $r_e = 1.198$ (1.207) Å, $D_e = 4.73$ (5.21) eV. Experimental values within parenthesis.

Key words: MCSCF — Correlation — Effective potential

1. Introduction

It is well known that inclusion of dynamic correlation effects is crucial for a proper quantitative description of the chemical bond. Using, for example, MCSCF theory it is possible to construct wave functions which give a qualitatively correct description of the electronic struture in a molecular system, also in situations where bond breaking or bond formation occurs. Such a theory can therefore overcome the obvious failures of the SCF theory.

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The MCSCF theory accounts for the near-degeneracy effects in the wave function and in this way includes what could be called long range correlation [1]. The MCSCF wave function is characterized as a configurational expansion comprising a limited number of configurations, where the occupied (internal) orbitals normally are obtained as bonding or anti-bonding combinations of atomic valence orbitals. Such wave functions allow, in contrast to the SCF method, for a proper description of asymptotic limits of energy surfaces, degeneracy effects occurring along paths for chemical reactions, etc. Special cases, which are well treated by MCSCF theory, are the atomic near-degeneracy effects occurring in atoms like for example Be ($2s^2 \rightarrow 2p^2$), where a two-configurational wave function accounts for 95% of the correlation energy of the 2s electron pair.

The MCSCF method is today an established method for studying molecular systems. A special version is the complete active space (CAS) SCF method, where the selection of important configurations is avoided and it is only necessary to specify an internal orbital space [2, 3].

While the MCSCF method is capable of a qualitatively correct description of chemical binding, it does in general not give quantitatively accurate results. Dynamic, or short range, correlation effects account for a non-negligible fraction of bond energies. A good example is N_2, where about 90% of the dissociation energy can be accounted for by MCSCF wave functions [2]. The remaining (0.8–0.9 eV) part can be attributed to short range correlation. In *ab initio* quantum chemistry these effects are normally accounted for by the configuration interaction (CI) method [4]. Often very accurate results can be obtained with the CI method, and it is today used in a variety of applications to different problems in chemistry and chemical physics. The CI method is, however, limited by the number of configurations that can be used in the expansion of the wave functions. Since the convergence is slow in this linear expansion method a very large number of terms is often needed. A good example is given by Cr_2, where it has been estimated that more than 50×10^6 configurations would be needed in order to account for the multiple bonding in the molecule [5]. For larger systems containing many electrons the problem becomes even worse due to the increasing difficulties in handling the cluster effects.

Dynamic correlation manifests itself in chemical bonds mainly as intra-atomic correlation. It is the ionic terms in the wave-function, which cannot be properly treated on a low level of theory (SCF or MCSCF). The energy of these terms are consequently too high and resulting binding energies become too small. Goodgame and Goddard [6] have introduced semiempirical correction terms in the two-electron integrals in order to reduce the error in describing atomic electron affinities. Applying these corrections in conjunctions with the GVB (generalized valence bond) method accurate potential curves were produced for some diatomic molecules, among them Cr_2. The possibility to describe electron correlation empirically by reducing the values of the two-electron integrals was exploited 20 years ago by Clementi [7], who modified the Coulomb integrals by breaking of integration at a given small interelectronic distance. This distance was estimated empirically for the He atom, and was then used in calculations on other atoms and some molecules. The correlation energy computed in this way was in reasonable agreement with experimental evidence.

Ruedenberg and coworkers have recently presented a method, where empirical intra-atomic correlation corrections are introduced by transforming a FORS wave function into a linear combination of antisymmetrized products of atomic state functions [8]. It is shown in their work that the intra-atomic correlation effects are to a large extent responsible for the errors obtained e.g. dissociation energies in calculations using the FORS (full valence CASSCF) model.

The idea of treating dynamic correlation effects by reducing the Coulomb repulsion term in the Hamiltonian also forms the basis for the present work, however, in a more advanced form than the one suggested by Clementi and Goodgame. An effective potential is added to the Hamiltonian, which should reflect the nature of the Coulomb hole. The modified Hamiltonian is used in conjunction with the CASSCF method. The wave function is thus allowed to relax in the presence of the correlation potential. This is an important aspect of the present method, in contrast to several previous attempts, where a correlation correction is added to the energy only, without affecting the wave function. Relaxation of the electron density due to dynamic correlation effects is, important in many systems, especially those which contain transition metal atoms [9]. Such relaxation is also included in the intra-atomic correlation corrected FORS model of Ruedenberg et al. [8].

2. The effective potential

An effective correlation potential can formally be derived from a wave function of the form

$$\psi = C\phi, \tag{1}$$

where C is a correlation factor and ϕ is an approximate (for example SCF or CASSCF) wave function. Inserting (1) into the Schrödinger equation leads after some simple manipulation to

$$(\mathcal{H} + C^{-1}[\mathcal{H}, C])\phi = E\phi, \tag{2}$$

where E is the exact energy corresponding to the Hamiltonian $\mathcal{H}$. The effective potential may thus be defined as

$$\mathcal{V}_{\text{eff}} = C^{-1}[\mathcal{H}, C]. \tag{3}$$

Essén [10] has recently explored this form of the effective potential and suggests several forms, where in the most simple version $\mathcal{V}_{\text{eff}}$ is given as a sum of delta functions. Blomqvist and Essén [11] have used this form to study electron correlation in some closed shell atoms.

The major problem in using (3) to construct an effective potential is to find a suitable form of the correlation factor C. Some hints may be obtained from a method proposed by Colle and Salvetti [12, 13], who calculated the correlation energy using reduced, second-order density matrices. The correlation factor used by them [12] fulfills the cusp condition and has the form

$$C=\prod_{i<j}(1-\varphi(\boldsymbol{r}_i,\boldsymbol{r}_j)), \tag{4}$$

where the two-electron function φ is given as

$$\varphi(\boldsymbol{r}_i,\boldsymbol{r}_j)=\exp(-\beta^2 r_{ij}^2)(1-f(\boldsymbol{R})(1+r_{ij}/2)), \tag{5}$$

where $\boldsymbol{R}=(\boldsymbol{r}_i+\boldsymbol{r}_j)/2$. The parameter β was assumed to be proportional to the third root of the local electron density ρ, $\beta=q\rho(\boldsymbol{R})^{1/3}$. The coefficient q was determined empirically, and the function $f(\boldsymbol{R})$ was approximated.

Substitution of the correlation factor (4) into (3) leads to a too complicated effective potential to be of practical use. Further simplifications are necessary. Under certain conditions $f(\boldsymbol{R})$ can be determined as a solution to a differential equation [14]. Assuming this function to depend only weakly on $\boldsymbol{R}$ it is straightforward to show that for small inter-electronic distances the leading term of the effective potential has the form:

$$\mathscr{V}_{\text{eff}}=-\mu\sum_{i<j}\exp(-\nu r_{ij}^2)/r_{ij}. \tag{6}$$

The parameters μ and ν here have a simple interpretation as the depth (μ) and the radius (ν^{-2}) of the Coloumb hole generated by $\mathscr{V}_{\text{eff}}$. The form (6) for $\mathscr{V}_{\text{eff}}$ is especially convenient in conjunction with gaussian basis sets. Two-electron matrix elements may easily be generated by a slight modification of the gamma function in existing two-electron integral codes. Here the MOLECULE integral program has been used for this purpose [15].

Ideally the parameters μ, and ν in (6) should be assumed to be functions of the local density $\rho(\boldsymbol{R})$. This is obviously not possible if the relative simplicity of the potential is to be retained. In the atomic case μ and ν have instead been chosen as functions of the average electron density:

$$\bar{\rho}=\int\rho^2(\boldsymbol{R})\,d\boldsymbol{R}\Big/\int\rho(\boldsymbol{R})\,d\boldsymbol{R}. \tag{7}$$

It is clear that an ansatz for the effective potential in the simplified form given above can only approximately account for the dynamical correlation effects. It can only be defended by showing its strength in applications. It is also necessarily empirical, since the parameters that determine μ and ν must be obtained from empirical estimates of the correlation energy in some test systems. The major virtue with the present approach lies in the effective Hamiltonian approach, which allows the approximate wave function to relax under the influence of the correlation term. The approach is in this sense similar to the work by Ruedenberg et al. [8] and Goodgame and Goddard [6], and in contrast to, for example the work by Colle and Salvetti [12, 13], where the correlation energy only is estimated from a fixed one-electron density which is normally computed from an SCF or small MCSCF wave function. It is also important to emphasize that only the short-range correlation effects are to be treated through $\mathscr{V}_{\text{eff}}$. Near degeneracy effects are included in ϕ through the CASSCF procedure.

3. Determination of the parameters μ and ν

In order to study the behaviour of the correlation energy as a function of the parameters in the effective potential, a series of full valence CASSCF calculations were performed on the first row atoms in their ground state. These calculations are single configurations for all atoms except Be (^1S), B(^2P), and C(^3P), where the 2s–2p near degeneracy influences the wave function. The calculations did not include correlation of the 1s-shell (except for He). For all systems studied the computed correlation energy could be fitted to the empirical value [16] for values of μ and ν fulfilling a linear relation:

$$\mu = \mu_0 + p\nu, \tag{8}$$

where the parameters μ_0 and p are different for each electronic state of an atom or ion. The accuracy of the linear dependence (8) is illustrated in Fig. 1, for the ground state atoms B–Ne. The computed points in this figure corresponds to μ, ν values for which the calculated valence correlation energy agrees with the empirical value. The three points given for each atom are seen to lie on an almost perfectly straight line. The errors obtained in the correlation energies using equation (8) were less than 0.1% in the region $\nu = 0.0$–0.5. This error is considerably smaller than the errors obtained in the parametrization of μ and ν discussed below, and Eq. (8) could therefore be used as the basis for this parametrization. The fitted values of μ_0 and p are given in Table 1 for the first row ground state atoms, and also for some ions.

A functional dependence of μ and ν on the average electron density $\bar{\rho}$ was assumed in the form:

$$\mu = x_1 \bar{\rho}^{x_2}, \tag{9}$$

$$\nu = (x_3 + \Delta x_4)\bar{\rho}^{x_5}. \tag{10}$$

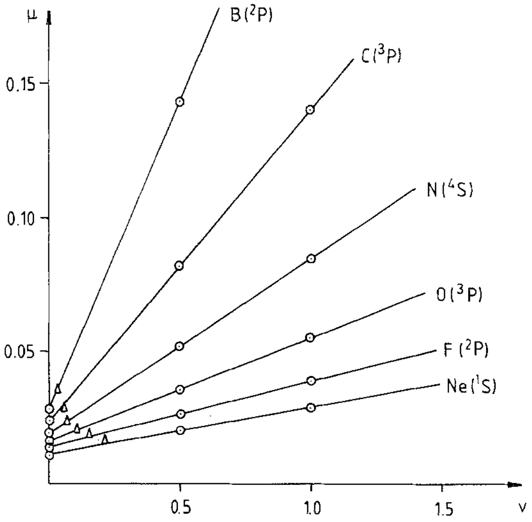

Fig. 1. The linear relation (8) illustrated for the atoms B–Ne. ⊙: μ, ν values for which the computed correlation energy agrees with the empirical values. Δ: μ, ν values obtained from Eqs. (9) and (10)

Table 1. The parameters μ_0 and p in Eq. (8)

Atom	μ_0	p
He(^{1}S)	0.0408	0.0463
Be(^{1}S)	0.0076	0.1860
B(^{2}P)	0.0284	0.2306
C$^+$(^{2}P)	0.0209	0.0879
C(^{3}P)	0.0245	0.1188
C$^-$(^{4}S)	0.0256	0.1539
N(^{4}S)	0.0197	0.0652
O$^+$(^{4}S)	0.0152	0.0317
O(^{3}P)	0.0165	0.0389
O$^-$(^{2}P)	0.0186	0.0515
F(^{2}P)	0.0140	0.0252
Ne(^{1}S)	0.0119	0.0171

The numbers $x_1 - x_5$ are treated as universal constants and are determined through a minimization of the least square errors of (8) for the ground state atoms:

$$S = \sum_{i}^{\text{atoms}} \left(x_1 \bar{\rho}_i^{x_2} - \mu_{0i} - p_i(x_3 + \Delta_i x_4)\bar{\rho}_i^{x_5}\right)^2, \tag{11}$$

where $\bar{\rho}_i$ is the average density for atom i, computed using the initial CASSCF wave function.

The parameter Δ occurring in (10) is introduced to account for the amount of correlation already introduced into the CASSCF wave function. In principle the radius of the Coulomb hole should go to zero when ϕ approached the exact wave function. Δ should measure this by increasing when a more exact form of ϕ is used. For SCF wave functions Δ is assumed to be zero. A simple form of this correlation parameter has been suggested by Colle and Salvetti [13]. Here we propose a slightly modified expression, which is easier to evaluate with the computational software available to us:

$$\Delta = (A/C - A_{\text{SCF}}/C_{\text{SCF}})^2, \tag{12}$$

where A and C are obtained as

$$A = \int_{\boldsymbol{r}_1 = \boldsymbol{r}_2} \{(\boldsymbol{h}(1) + \boldsymbol{h}(2))P_2(1, 1'; 2, 2')\}_{1=1'2=2'} \, dV \tag{13}$$

and

$$C = \int P_2(1, 1, 1, 1) \, dV. \tag{14}$$

As shown by Colle and Salvetti, the integrand in (13) approaches infinity for $\boldsymbol{r}_1 = \boldsymbol{r}_2$ when the second order reduced density matrix P_2 becomes exact. The integrated form (13) can easily be evaluated in a molecular orbital basis by introducing a new set of two-electron integrals:

$$N_{pqrs} = \int \varphi_p(1)\varphi_q(1)\varphi_r(1)\varphi_s(1) \, dV_1. \tag{15}$$

These integrals are also needed for the evaluation of the average density (7). They can be easily calculated using the formalism derived for calculations of two-electron integrals over Gaussian type functions [17, 18]. The same type of integrals were used by von Niessen in a localization procedure for molecular orbitals [19].

The coefficients μ_{oi} and p_i from the linear relation (8) for the atoms B, C, O, N, F, and Ne were used to determine the parameters x_1–x_5. For B and C multiconfigurational wave functions were used. The values of the parameter Δ obtained for these two atoms were used 0.026 and 0.029. Hartree-Fock (or CASSCF for B and C) values for $\bar{\rho}$ were used. It could be argued that this parameter should be allowed to relax under the effect of $\mathcal{V}_{\text{eff}}$, which would result in an iterative procedure for the calculation of the parameters x_1–x_5. Such a procedure would, however, lead to only very small changes in the computed values, since the effect of $\mathcal{V}_{\text{eff}}$ on $\bar{\rho}$ is small. The values obtained for the universal parameters x_1–x_5 are as follows:

$$x_1 = 0.01256,$$
$$x_2 = -0.2293,$$
$$x_3 = 0.4991,$$
$$x_4 = 7.999,$$
$$x_5 = 0.6766.$$

It is interesting to notice that the fitting procedure results in a value for x_5 which is very close to the value 2/3, the value used by Colle and Salvetti [12], and is the value required using dimensionality arguments. The μ, ν values computed from Eqs. (9) and (10) are given by the small triangles in Fig. 1 for the atoms B–Ne, illustrating the closeness of these fitted μ, ν values to the ideal values (the straight lines).

The correlation energy for a number of first row atoms, positive and negative ions was computed using these parameter values. Extensive 2s, 2p basis sets were used in these calculations to avoid contamination of the results from basis set deficiencies. The resulting CASSCF and correlation energies are given in Table 2. Note that for B, C, C^+, and N^+ the quoted correlation energies are the energy differences with respect to the CASSCF energy (full valence MCSCF) and not to the SCF energy. The effective potential method seems to be able to reproduce the valence correlation energy to within 10% in most cases. However, even such a relatively small error can represent an appreciable amount of energy and can lead to sizeable errors in calculations of energy differences. A first check can be obtained by using the results of Table 3 to compute ionization potentials and electron affinities. Considerable improvement is obtained compared to the CASSCF (SCF) values. The results, however, still differ from experiment with in some cases more than 0.7 eV.

The method has also been tested in calculations on some small molecules. Basis sets of triple zeta quality plus two polarization functions on each centre were

Table 2. CASSCF and correlation energies for a number of first row atoms and ions (atomic units)

Atom	CASSCF energy	Valence correlation energy[a]	
		$\mathcal{V}_{\text{eff}}$	empirical[b]
$B(^2P)$	−24.5663	−0.0374	−0.0367
$C(^3P)$	−37.7075	−0.0772	−0.0791
$N(^4S)$	−54.4007	−0.1297	−0.1270
$O(^3P)$	−74.8110	−0.1915	−0.1855
$F(^2P)$	−99.4099	−0.2635	−0.2494
$Ne(^1S)$	−128.5464	−0.3470	−0.3178
$C^+(^2P)$	−37.3348	−0.0326	−0.0379
$N^+(^3P)$	−53.9103	−0.0852	−0.0830
$O^+(^4S)$	−74.3723	−0.1410	−0.1237
$F^+(^3P)$	−98.8328	−0.2057	−0.1863
$Ne^+(^2P)$	−127.8181	−0.3098	−0.2538
$C^-(^4S)$	−37.7074	−0.1144	−0.1204
$O^-(^2P)$	−74.7912	−0.2394	−0.2592
$F^-(^1S)$	−99.4554	−0.3191	−0.3306

[a] This correlation energy does not include the $(2s)^2 \rightarrow (2p)^2$ near degeneracy effect, which is included in the CASSCF energy

[b] Estimated from the data given in [16]

Table 3. Atomic ground state ionization potentials (IP) and electron affinities (EA) in eV

Atom		IP	ΔIP	EA	ΔEA
C	CASSCF	10.14	−1.11	−0.002	−1.12
	$\mathcal{V}_{\text{eff}}$	11.36	0.11	1.01	−0.11
	Exp.	11.25	—	1.12	—
N	CASSCF	13.34	−1.20		
	$\mathcal{V}_{\text{eff}}$	14.56	0.02		
	Exp.	14.54[a]	—		
O	CASSCF	11.94	−1.67	0.54	−0.93
	$\mathcal{V}_{\text{eff}}$	13.31	−0.30	0.76	−0.71
	Exp.	13.61[a]	—	1.47[b]	—
F	CASSCF	15.71	−1.71	1.24	−2.21
	$\mathcal{V}_{\text{eff}}$	17.26	−0.16	2.75	−0.70
	Exp.	17.42[a]	—	3.45[b]	—
Ne	CASSCF	19.82	−1.74		
	$\mathcal{V}_{\text{eff}}$	20.83	−0.73		
	Exp.	21.56[a]	—		

[a] [20]

[b] [21]

Table 4. Calculated bond lengths and dissociation energies for the molecules H_2, N_2 and O_2

		R_e (Å)	ΔR_e (Å)	D_e (eV)	ΔD_e (eV)
$H_2(^1\Sigma_g^+)$	CASSCF	0.755	0.014	4.13	−0.62
	$\mathcal{V}_{\text{eff}}$	0.745	0.004	4.62	−0.13
	Exp.[a]	0.741	—	4.75	—
$N_2(^1\Sigma_g^+)$	CASSCF	1.108	0.010	8.99	−0.92
	$\mathcal{V}_{\text{eff}}$	1.099	0.001	10.42	0.51
	Exp.[a]	1.098	—	9.91	—
$O_2(^3\Sigma_g^-)$	CASSCF	1.222	0.015	3.91	−1.30
	$\mathcal{V}_{\text{eff}}$	1.198	0.009	4.73	−0.48
	Exp.[a]	1.207	—	5.21	—

[a] [22]

used. Again, full valence CASSCF calculations were performed with and without the effective correlation term in the Hamiltonian. Appropriate values for the parameters μ and ν were obtained using the average of the average densities of the free atoms. The results are given in Table 4. A considerable improvement in computed bond distances and bond energies is obtained for all the three molecules studied.

4. Conclusions

This idea behind this work is simple and pragmatic: is it possible to devise an effective potential method, which accounts for the dynamic correlation effects, and which can be implemented into an MCSCF method without increasing the computational effort too much? The experience gained in the present first attempt to achieve this goal is positive. The effective potential employed is easily included into existing software, and the only additional computational step is the calculation of the integrals (15). On the other hand the results obtained are not accurate enough to defend large scale applications of the method at the present stage.

The most serious problem is the dependence of the effective Hamiltonian on the electron density. In an LCAO framework it is not possible to let the parameters depend on the local density, which would lead to two-electron integrals that could only be computed numerically. The approach taken here to use an averaged density is, however, not entirely satisfactory, especially not in molecules. In the test examples used here (homonuclear diatomics) appropriate μ and ν values could be obtained using averaged atomic densities. In heteronuclear systems such a simplified approach cannot be used. It is then necessary to extend the method such that different densities are used in different parts of the system. This may be achieved by a transformation of the molecular orbitals of a CASSCF wave function to localized orbitals, calculating effective atomic densities from these orbitals, and use these densities to construct an effective potential for each atomic centre. Only one centre contributions to the potential would be included in the energy expression.

We feel that the present work can be used as a starting point in a search for simple, empirical, methods which accounts for the small, but chemically important, dynamic correlation effects in molecular systems.

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