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Extension of a simplified method for molecular correlation energy calculations to molecules containing third row atoms. I. Methodological developments

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An extension of a simplified method for molecular correlation energy calculations to molecules containing third row atoms is presented. In addition to the use of pseudo-potentials in the calculations, the consequences of this extension on the different components of the energy partition which is the basic idea of the method, is analysed. Particular emphasis is placed on the specific role played by the $3d$ orbitals in each of the energy components. First, at the zeroth order, the energy is found to be very sensitive to the optimization of the $3d$ polarization functions. Secondly, the internal correlation energy, calculated by CI, requires the optimization of distinct $3d$ correlation orbitals to describe adequately the strong near-degeneracy effects that occur within the valence space. Finally it is shown that the $3d$ orbitals contribute partially to the non-internal correlation energy and that, the "atoms-in-molecule" structures corresponding typically to all-external contributions are negligible. The concept of error energy is introduced in place of the non-internal correlation energy: it includes the relativistic contributions within the semi-empirical tables. Such tables are presented for second row atoms and for the chlorine atom. From these tables, predicted values for some atomic term energies, experimentally undetermined, are derived. The methodological tests are limited here to the chlorine atom which is chosen for further applications in the next paper of this series. The conclusions concerning the applicability of the method to third row atoms are however quite general.

Key words: Correlation energy—third row atoms—chlorine atom—pseudopotentials—atomic term energies—*ab initio* calculations

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1. Introduction

In a series of recent papers [1-6] we have developed and extensively tested a simplified method for molecular correlation energy calculations. The basic idea of the method is that the large configuration interaction expansions, generally encountered in the traditional approaches of the correlation problem, can be avoided by defining an appropriate partition of the correlation energy. The two components of the partition have been shown to be calculable in an economical way: the first one (internal correlation energy) is calculated by means of MCSCF/CI calculations performed on short configurational expansions and the second one (non-internal correlation energy) is determined by a semi-empirical "atoms-in-molecule" approach.

Up to now various tests and applications have been presented with successful comparison with other *ab initio* calculations and with experimental work. These results concern the calculation of potential energy hypersurfaces [4], dissociation and term energies [1, 2, 3, 4], heats of reactions [5], equilibrium geometries and vibrational frequencies [2, 4]. The systems considered so far were limited to atoms of the second row and hydrogen atoms, with typically up to 4 second row atoms and up to 30 electrons.

The success encountered in this previous work encourages us to extend the application area of the method to molecules containing third row atoms and to show, as suggested by preliminary results [6], that this extension does not affect the reliability and the economical character of the method. Although the development of the methodology is quite general, and therefore independent of the choice of a particular atom, we will herein restrict ourselves to numerical applications involving the chlorine atom only. This choice is governed by the chemical importance of most molecules containing this atom.

A first paper (I) is devoted to the methological implications of the extension and to the determination of the necessary numerical data for the chlorine atom. A second paper (II) presents test calculations on chlorinated molecules as ClO, HCl, HCl^+ and NCl.

2. The simplified method for molecular correlation energy calculations

In this section we give the guidelines of the method presented in detail in the previous papers [1-6]. The basic concepts of the method are: the partitioning of the orbital space into valence[1] and non-valence spaces and the subsequent classification of the orbital excitations (limited to the first order of perturbation, i.e. the biexcitations) into two classes: i) excitations within the valence space, corresponding to *internal correlation energy* contributions and ii) biexcitations in which one or two components leave the valence space, referred to as *non-internal correlation energy* contributions. An adequate choice of the zeroth-order wavefunction (Ψ_0) is of course crucial in order to ensure a proper description

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[1] The valence space is also referred to as the "H.F. sea". [7]

of the considered molecular process. This generally implies the use of a multiconfigurational zeroth-order wavefunction [2].

The total energy of the system is therefore approximated by the following partition:

$$E \sim E_0 + E^{\mathrm{I}}_{\mathrm{CORR}} + E^{\mathrm{NI}}_{\mathrm{CORR}} \tag{1}$$

where E_0 refers to the energy of the zeroth-order wavefunction $E^{\mathrm{I}}_{\mathrm{CORR}}$ and $E^{\mathrm{NI}}_{\mathrm{CORR}}$ to the internal and non-internal correlation energies respectively.

The size of the internal configuration space is relatively small so that a variational treatment (MCSCF/CI) of the internal correlation energy is possible. Oppositely, the very large size (in principle infinite) of the non-internal configuration space justifies the use of a semi-empirical "atoms-in-molecule" approach for this part of the correlation energy. It consists of expanding the zeroth-order wavefunction into a linear combination of products of atomic eigenfunctions and of expressing the molecular non-internal correlation energy as a weighted sum of the corresponding atomic non-internal correlation energies, these last quantities being accurately determined by semi-empirical calculations. The procedure of this atomic expansion of the molecular wavefunction is detailed in Ref. [2] and also discussed in Ref. [6].

3. Basis sets and pseudo-potentials

3.1. Basis set requirements of the method

We have shown in previous work that each term of the partition (1) is characterized by a specific basis set effect, and have drawn the following conclusions:

i) the zeroth-order energy E_0 is very sensitive to basis set effects and therefore an extended basis set of double zeta plus polarization quality is required to produce meaningful results

ii) the internal correlation energy $E^{\mathrm{I}}_{\mathrm{CORR}}$ can be calculated in the same extended basis set as E_0 providing that an iterative MCSCF/CI procedure is performed to ensure a complete optimization of the valence orbitals. The computation cost of this iterative procedure rather suggests the use of a minimal basis set, which is, by definition, a purely valence basis and therefore does not require a major optimization [2].

The internal correlation energy is thus calculated as the CI energy increment obtained with the minimal basis set, i.e.:

$$E^{\mathrm{I}}_{\mathrm{CORR}} = E_{\mathrm{MC_0(min)/CI(min)}} - E_{\mathrm{MC_0(min)}}$$

where the notation $\mathrm{MC_0(min)/CI(min)}$ has been introduced to designate the following two-step procedure: an MCSCF calculation is first performed on the zeroth-order multiconfigurational wavefunction and secondly a CI calculation is performed on the complete internal configuration space with the orbitals optimized in the first step. The same minimal basis set is used in the two steps.

iii) The univocal correlation that exists between basis orbitals and atomic valence orbitals imposes the use of a minimal basis set for the non-internal "atoms-in-molecule" calculations. The same basis set as that for the internal correlation energy calculations is chosen.

Up to now, Pople's standard basis sets have been used for second row atoms applications, i.e. the 6-31G$_{(**)}$ extended basis set [8] and the STO-3G minimal basis set [9]. However, as described in the next sections, the introduction of pseudo-potentials in our calculations requires the use of appropriate basis sets.

3.2. Pseudo-potentials

The increase in the number of core electrons with the third row atoms justifies the use of a pseudo-potential method in order to replace the "all-electron" variational problem by a "valence electrons" problem of reduced size. Extensive work in the literature has shown [10] that this approximation does not appreciably affect the accuracy of the results, as long as the molecular process under study does not disturb, of course, the electronic distribution of the inner shells.

Here we have adopted the pseudo-potential approach developed by Durand and Barthelat [10a, 11]. The pseudo-potential operator has the following semi-local form:

$$W_{PS} = \frac{-Z_{\text{eff}}}{r} + \sum_{l} W_l(r) P_l$$

where

$$P_l = \sum_{m=-l}^{+l} |Y_{lm}\rangle\langle Y_{lm}|$$

is the angular projection operator over the l^{th} sub-space of spherical harmonics, and

$$W_l(r) = e^{-\alpha_l r^2} \sum_{i=1}^{n} C_{i,l} r^{n_{i,l}}.$$

Numerical values for the parameters appearing in this last expression are tabulated in Ref. [12].

3.3. Valence basis sets for pseudo-potential calculations

In this work we have used the valence basis sets given in Ref. [12] optimized in atomic pseudo-potential calculations, with 4*s* and 4*p* gaussian primitives expansions. Two types of contractions are introduced: i) a complete contraction of the *s* and *p* components leading to a minimal basis set and ii) a contraction of the four *s* and *p* components into a (3 + 1) expansion leading to a double zeta quality basis set. Polarization and correlation 3*d* functions are optimized in this work, as discussed in Sect. 5.1 and 5.2.

4. Programs

The following programs have been used in this work:

i) the ALIS package written by Ruedenberg et al. [13] to perform MCSCF/CI calculations. We have extended this program to pseudo-potential calculations by using the routines of the PSHONDO program [14], that evaluate the monoelectronic integrals including the pseudo-potential contributions. CI calculations have been performed either by inserting [15] in ALIS the configurations generator program of the MELD CI program [16] or by using the Whitten's program [17] to set up the CI matrix together with the Davidson diagonalization routines [18];
ii) the program PSATOM [19] to optimize atomic basis sets;
iii) the numerical atomic multiconfigurational program written by Froese-Fischer [20];
iv) the program DINGO written by us to perform non-internal or error energies calculations.

5. Extension of the method to molecules containing third row atoms

5.1. Zeroth order wavefunction

In Sect. 3 we pointed out the necessity to use an extended polarized basis set to calculate the zeroth-order energy. Such basis sets can be derived from the tables of Ref. [12] (see Sect. 3.3), however polarization functions are to be optimized, since they are not available (except for Na, Si and P).

Although the M-shell is occupied for third row atoms, several calculations [21] show that polarization effects can be efficiently introduced by d orbitals. In fact, f orbitals are mainly requested to polarize δ orbitals which are never occupied in the zeroth-order wavefunctions used here. The technique that we have adopted for optimizing the polarization orbitals is to independently vary the different parameters of these orbitals and to fit their energy dependence by a polynomial expression. In Table 1 we present a comparison of the efficiency of different polarization functions at the SCF and MCSCF levels of calculation, in order to choose for further calculations, a basis set which presents a suitable compromise between the polarization energy lowering (ΔE) and the relative computation time

Table 1. Influence of the d polarization functions on energy (ΔE) and relative CP calculation time (T_{rel})

ClO($^2\Pi$)	n_g(O)	n_g(Cl)	ΔE(eV)	T_{rel}
SCF at 3.0 a.u.	0	0	0.00	1.0
	1	1	1.67	6.3
	1	2	1.76	10.0
	2	2	1.80	18.0
MCSCF at 3.2 a.u.	0	0	0.00	3.6
	1	2 (cont.)	0.97	11.0

Table 2. Parameters of the optimized $3d$ polarization functions

Atom	Optimized on	ξ_1	ξ_2	c_1 [a]	c_2 [a]
Cl	ClO	0.77	—	1.0	—
		0.77	0.25	1.0	0.5
Cl	HCl^+	0.80	0.21	1.0	0.8
Cl	HCl	0.70	0.21	1.0	0.6
O	ClO	0.86	—	1.0	—
N	NCl	0.67	—	1.0	—

[a] Contraction coefficients are given for the unnormalized orbitals

(T_{rel}). The $3d$ functions are characterized by the number of Gaussian primitives (n_g) which are contracted (cont.) or not. On the basis of the results of Table 1, we decided to adopt a one Gaussian $3d$ function on the oxygen atom and one two-primitives contracted function on the chlorine atom. The introduction of a second Gaussian on the chlorine and not on the oxygen atom can be justified by the fact that the corresponding polarization energy lowering is a factor of two greater for the chlorine (0.09 eV) than for the oxygen (0.04 eV). This last value lies at the limit of precision of our calculated energy differences and does not justify the use of 80% extra computation time. We have also decided to contract the two chlorine Gaussian functions in order to decrease the MCSCF computation time, which is very sensitive to the size of the basis set.

The polarization introduced in this way ($\sim$1 eV) leads to an increase of the MCSCF time of a factor of three with respect to the reference calculation performed without polarization orbital.

Finally, in Table 2 we present the parameters of the d-polarization orbitals for O, N and Cl atoms, optimized on the ClO, NCl, HCl and HCl^+ molecules. For the chlorine atom, we compare the results of the optimization carried out on the ClO, HCl and HCl^+ molecules; as can be seen, the parameters of these orbitals are very close. Moreover, the energy dependence of these parameters is very slight. Therefore, we obtain the usual result that the polarization functions are not very sensitive to the chemical environment of the atom on which these functions are centered. We can thus consider these orbitals as transferable. This transferability is achieved even in the case where charge transfers occur, as for instance when going from HCl to HCl^+. Indeed, we observe a lowering of the equilibrium energy of HCl^+ of only 0.02 eV by optimizing the $3d$ orbital on HCl^+ itself in place of HCl. Henceforth, it is the orbital optimized on ClO that will be used in further calculations.

5.2. Internal correlation energy

As a consequence of the definition introduced in Sect. 2, the internal correlation energy ($E^{\mathrm{I}}_{\mathrm{CORR}}$) of an atom or a molecule is obtained by diagonalisation of the Hamiltonian in the configurational space spanned by all the mono and biexcitations within the so-called "valence-space" with respect to a given reference (the zeroth-order wavefunction). The internal correlation energy corresponds to the near-degeneracy energy of orbitals belonging to the same shell (i.e. orbitals $2s$ and $2p$ for the shell $n=2$ of second row atoms). For third row atoms, the near-degeneracy complex (Layzer complex) $n=3$ contains the orbital $3s$, $3p$ and $3d$ so that it is also necessary to optimize $3d$ correlation orbitals if one wishes to calculate the internal correlation energy of these atoms as well as that of the molecules of which they are part. The optimization of the correlation orbital is carried out in the same manner as it was for the polarization orbital (see Sect. 5.1).

This orbital added to the completely contracted set [12] will provide the minimal basis set required for this step of the calculation.

5.2.1. Molecular optimization of a $3d$ correlation orbital

The $3d$-correlation orbitals have been optimized by minimizing the energy corresponding to the CI calculation performed on the internal correlation configurational space. Test calculations have been carried out on the ground $^2\Pi$ state of the ClO molecule, near its equilibrium geometry. However, since we don't have any reference value for the internal correlation energy of the ClO molecule, we calculated with the same basis set, for each optimized correlation orbital, the internal correlation energy of the chlorine atom in the ground ^{2}P state.

This value was compared with the very accurate result obtained by means of a numerical MCHF calculation performed on the whole near-degeneracy complex of the atom, in order to test the quality of the optimized correlation orbital.

In Table 3 and in Fig. 1 we present the evolution of the internal correlation energy of the chlorine atom calculated in the minimal basis set (MB) as a function of the quality of the $3d$ correlation orbital optimized on the ClO molecule. One can see that if this orbital is represented with the help of one Gaussian primitive (MB4), we can already calculate 90% of the reference (numerical) value. Similarly to what was done for the polarization orbital, we optimized a correlation orbital formed by a contraction of two Gaussian primitives (MB5). It only leads to a slight relative improvement (~4%) of the calculated internal correlation energy of the chlorine atom, but it lowers the absolute value by an amount of 0.1 eV, what is appreciable. We consider this final result as very satisfying and admit that the internal correlation energy of the ClO molecule is similarly approached, as suggested by the parallel evolution of the internal correlation energy of Cl and ClO along with the quality of the optimized correlation orbital illustrated in Fig. 1.

There are also two other correlation orbitals for the chlorine atom presented. The first one (MB2) is an attempt to obtain such an orbital by using the option for basis set optimization of PSATOM. The method would have the advantage of very easily giving a correlation orbital without performing CI calculations. Since no $3d$ orbital is occupied in the ground state configuration of the chlorine atom, we arbitrarily decided to perform the calculation on the ^{4}F state of the KL $3s^2 3p^4 3d$ configuration. The very bad result obtained when we tried to

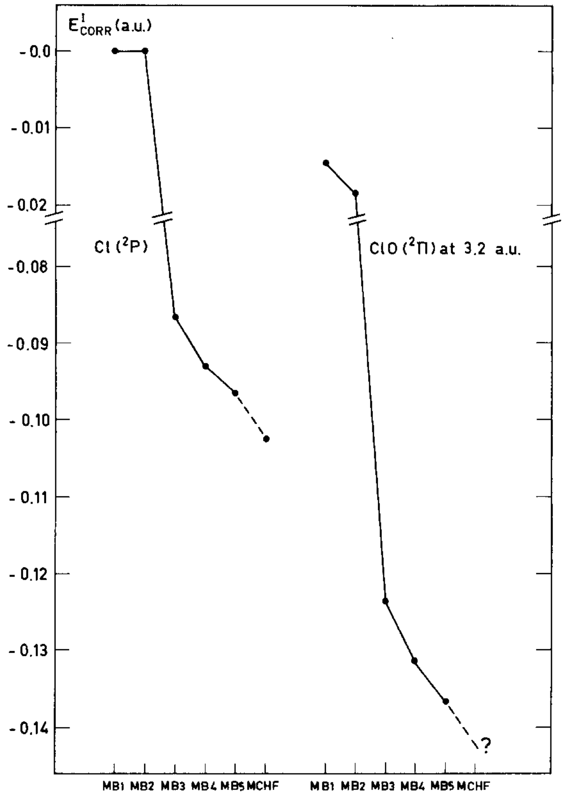

Fig. 1. Evolution of the internal correlation energy of Cl and ClO as a function of the quality of the 3*d* correlation orbital

Table 3. Calculated internal correlation energy (a.u.) of the chlorine atom as a function of the quality of the 3*d* correlation orbital

Minimal basis set (MB)[a]	Characteristic of the *d* correlation orbital[b]	$E^{I}_{CORR}Cl(^2P)$	%
MB1	without *d*	0.0000	0.0
MB2	atomic SCF	0.0002	0.2
MB3	polarization	0.0864	84.0
MB4	correlation ($n_g = 1$)	0.0928	90.0
MB5	correlation ($n_g = 2$)	0.0963	94.0
MCHF	numerical	0.1026	100.0

[a] Same notations as in Fig. 1

[b] See comments in the text

calculate the internal correlation energy of the chlorine atom with this orbital was predictable because of the well-known difference between SCF and correlation orbitals. The second one (MB3) is just the polarization orbital discussed in Sect. 5.1 which gives a reasonable approximation of the internal correlation energy of the atom due to the relative similarity that exists between SCF polarization and correlation orbitals [22].

We can conclude that we are able to obtain with MB5 a reliable molecular correlation orbital. However such a CI optimization on each molecule studied is long and expensive so that it would be very interesting to obtain a correlation orbital "transferable" i.e. usable in each molecular calculation without particular optimization.

5.2.2. Optimization of a transferable correlation orbital

By performing an atomic CI calculation we optimized in a first step a correlation orbital for the ^2P state of the chlorine atom. In a second step, we calculated with this orbital the internal correlation energy of the ClO, HCl and HCl^+ molecules and compared the values obtained therefrom with the ones obtained using the correlation orbital specifically optimized for these molecules.

The results of the calculations are presented in Table 4 where we indicate in the first column the molecule or atom whose internal correlation energy is calculated, in the second column the system on which the correlation orbital was optimized and finally in the third column the value (in a.u.) of the internal correlation energy.

For the HCl and ClO molecules, the perfect agreement between the values of the internal correlation energy calculated with both kinds of correlation orbitals, the ones optimized for the molecule and the one optimized for the atom, demonstrates the transferability of the latter.

Let us now turn to the results concerning the Cl^+ and HCl^+ ions. The comparison between the internal correlation energy of Cl^+ and HCl^+ calculated using a correlation orbital optimized on these species on the one hand and on Cl on the other hand shows that i) the correlation orbital optimized on Cl is relatively inadequate to calculate the internal correlation energy of the ionic species Cl^+ and HCl^+. For instance, for Cl^+ we can only calculate 82% of the reference value obtained through a numerical MCHF calculation; ii) an optimization on Cl^+

Table 4. Test of the transferability of $3d$ correlation orbital

Molecule	Optimization on	$E^{\mathrm{I}}_{\mathrm{CORR}}$(a.u.)
ClO $R = 3.8$ a.u.	Cl	0.1335
	ClO	0.1335
HCl $R = 2.4$ a.u.	Cl	0.1005
	HCl	0.1005
HCl^+ $R = 3.5$ a.u.	Cl	0.0906
	Cl^+	0.0985
	HCl^+	0.0988
Cl^+	Cl	0.0811
	Cl^+	0.0929
	—	0.0984 (MCHF)

Table 5. Parameters of the optimized $3d$ correlation functions

System	ξ_1	ξ_2	c_1[a]	c_2[a]
Cl	0.60	0.30	1.0	0.40
ClO	0.60	0.30	1.0	0.45
HCl	0.60	0.30	1.0	0.40
Cl^+	0.85	0.26	1.0	0.65
HCl^+	0.91	0.31	1.0	0.72

[a] The contraction coefficients are given for the unnormalized orbitals

leads to a correlation orbital that allows us to calculate 94% of the reference value for the internal correlation energy of Cl^+ and moreover, the comparison between the internal correlation energy of HCl^+ calculated with this orbital and with the one optimized on HCl^+ itself shows that it is perfectly transferable. We then possess $3d$ correlation orbitals that can be involved without reoptimization in calculations on chlorinated molecules or molecular ions.

Finally, in Table 5 we present the optimized $3d$ correlation orbitals for $Cl(^2P)$, $Cl^+(^3P)$, $ClO(^2\Pi)$, $HCl(^1\Sigma^+)$ and $HCl^+(^2\Pi)$. The great similarity between the correlation orbitals optimized on Cl, ClO and HCl on the one hand and on HCl^+ and Cl^+ on the other hand reflects the results of Table 4.

5.3. Non-internal correlation energy

The extension of the "atoms-in-molecule" method to molecules containing third row atoms requires a detailed investigation of the two following points: first, the effect of the inclusion of an additional valence orbital ($3d$ orbital) in the atomic expansion of the zeroth-order wavefunction and secondly the tabulation of the necessary semi-empirical atomic data. This last point implies the consideration of a new concept, the error energy, introduced in a previous paper [6] and discussed in detail hereafter.

5.3.1. Atomic expansion of the zeroth-order wavefunction

The addition of a $3d$ orbital in the H.F. sea, in addition to the $3s$ and $3p$ orbitals, substantially increases the number of possible "atoms-in-molecule" structures that arise from the expansion of the zeroth-order wavefunction. Typically, for a second row atom the K $2s^m2p^n$ configurations (with $m=0$ to 2 and $n=0$ to 6) can lead to only 256 (L, S, M_L, M_S) eigenstates whereas for third row atoms with KL $3s^m3p^n3d^l$ configurations (with $l=0$ to 10) this number becomes 262144. Obviously, the computation time involved in the "atoms-in-molecule" procedure grows significantly with the size of the atomic eigenfunctions space. In fact one of the most time consuming steps in this procedure is certainly the linear transformation that projects the cartesian atomic determinants basis set to the LS eigenfunctions basis set.

However, we think that this extra computation time can be saved without loss of reliability, by neglecting in the expansion the contributions of determinants in which $3d$ orbitals are occupied. In fact, the neglect of these contributions can be expected to be small as a consequence of the small occupation probability of the $3d$ orbitals in the molecular zeroth-order wavefunctions.

As an example, for the ClO molecule ($R = 2.7$ a.u.) only 6% of the chlorine atom contributions correspond to KL $3s^m 3p^n 3d^l$ structures (with $l \neq 0$), of which ~5% is equally distributed on the KL $3s^2 3p^3 3d$ and KL $3s^2 3p^4 3d$ configurations, 0.3% on the KL $3s^2 3p^2 3d$ configuration and less than 0.05% on the other ones. However it is important to point out that the approximation we just introduced is not to completely neglect the $3d$-contributions to the non-internal correlation energy. Indeed, two types of $3d$-contributions occur: i) *semi-internal* ones which consist in the biexcitation of one $3s$ or $3p$ electron to a $3d$ orbital and a second electron to a non-valence orbital. ii) *all-external* ones in which the two electrons involved in the biexcitations ($3d + 3s$, $3d + 3p$ or two $3d$ electrons) shift to the non-valence space.

The first contributions are not neglected here and in fact are taken into account by a part of the non-internal correlation energies of the KL $3s^m 3p^n$ configurations. These contributions are expected to be important as a consequence of the strong interactions that exist between the $3s$, $3p$ and $3d$ near-degenerated orbitals. Moreover the considered configurations are also expected to significantly contribute to the zeroth-order wavefunction expansion. It is the all-external contributions that we neglect, because they arise from configurations KL $3s^m 3p^n 3d^l$ which are, as mentioned above, not significantly occupied in the expansion of the zeroth-order wavefunction.

The numerical incidence of the neglect of these $3d$-occupied configurations on the non-internal correlation energies has been estimated to be less than 0.1 eV, this uncertainty lying within the numerical accuracy of the method.

5.3.2. Semi-empirical atomic data

The determination of the semi-empirical atomic data required for the calculation of the "atoms-in-molecule" correlation energies will be discussed in the next sections. It consists in the calculation of the non-internal correlation energies

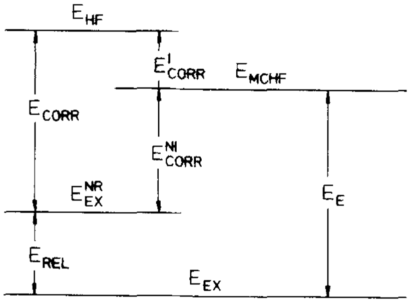

Fig. 2. Definition of non-internal correlation energy and error energy

corresponding to all the possible LS states arising from the neutral and ionic configurations of the considered atoms. As illustrated in Fig. 2, each of these calculations requires the knowledge of the corresponding *internal correlation energy* and of the *exact non relativistic energy.* These two energy components will successively retain our attention.

5.3.3. Atomic internal correlation energies calculations

By performing numerical MCHF calculations, we calculated the internal correlation energy for the states arising from neutral and ionic configurations of the chlorine atom.

The internal correlation energy of a given LS state resulting from a configuration Γ is defined as:

$$E^{\mathrm{I}}_{\mathrm{CORR}}(\Gamma\mathrm{LS}) = E_{\mathrm{MCHF}}(\Gamma\mathrm{LS}) - E_{\mathrm{HF}}(\Gamma\mathrm{LS})$$

where E_{MCHF} is the energy associated to the wavefunction:

$$\Psi_{\mathrm{MCHF}}(\Gamma\mathrm{LS}) = \sum_{\mathrm{complex}} c_i \Phi(\gamma_i \mathrm{LS}) \qquad (2)$$

where the summation goes over all the CSF's ($\Phi(\gamma_i\mathrm{LS})$) pertaining to the Layzer complex.

The results of the calculations are presented in Table 6. In a few cases, marked by an asterisk, very strong interactions occur in the MCHF calculations between two or three CSF's. As a consequence, we cannot say that the wavefunction (2) represents the internal correlation wavefunction of one given ΓLS state, the representation of an atomic state by one main configuration losing its sense. Let us take the following example. For the ^{2}S state arising from the $\mathrm{KL}\,3s3p^6$ configuration of Cl, the Layzer complex is formed by six CSF's. Two of them,

$$\Phi(\gamma_1\,{}^2\mathrm{S}) = |\mathrm{KL}\,3s(^2\mathrm{S})3\mathrm{p}^6(^1\mathrm{S});{}^2\mathrm{S}\rangle \qquad (3a)$$

$$\Phi(\gamma_2\,{}^2\mathrm{S}) = |\mathrm{KL}\,3s^2(^1\mathrm{S})3p^4(^1\mathrm{D})\{^1\mathrm{D}\}3d^1(^2\mathrm{D});{}^2\mathrm{S}\rangle \qquad (3b)$$

strongly interact and the diagonalization of the MCHF matrix gives for the first two roots and taking only into account the main weights:

$$\Psi_{\mathrm{MCHF}}(\Gamma_1\,{}^2\mathrm{S}) \simeq 0.802734\Phi(\gamma_1\,{}^2\mathrm{S}) + 0.572659\Phi(\gamma_2\,{}^2\mathrm{S}) \qquad (4a)$$

$$\Psi_{\mathrm{CI}^2}(\Gamma_2\,{}^2\mathrm{S}) \simeq 0.544424\Phi(\gamma_1\,{}^2\mathrm{S}) - 0.794771\Phi(\gamma_2\,{}^2\mathrm{S}). \qquad (4b)$$

So that following Kaufman [23], we should talk about the states $\binom{+}{+}$ and $\binom{+}{-}$ instead of the states $\Phi(\gamma_1\,{}^2\mathrm{S})$ and $\Phi(\gamma_2\,{}^2\mathrm{S})$.

The associated energies are:

$$E_{\mathrm{MCHF}}(\Gamma_1\,{}^2\mathrm{S}) = -459.1741\ \mathrm{a.u.}$$

$$E_{\mathrm{CI}}(\Gamma_2\,{}^2\mathrm{S}) = -458.7146\ \mathrm{a.u.}$$

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[2] This function is the second eigenvector of the interaction matrix constructed with the orbitals optimized for the $\Gamma_1\,{}^2\mathrm{S}$ state and hence cannot be a MC solution for the $\Gamma_2\,{}^2\mathrm{S}$ state

Table 6. Atomic data for the chlorine atom (a.u.)

Configuration	State	System	$-E_{\mathrm{EXP}}$	$-E_{\mathrm{HF}}$	$-E_{\mathrm{MCHF}}$	$-E^{\mathrm{I}}_{\mathrm{CORR}}$	$-E_{\mathrm{E}}$
KL $3s^2 3p^6$	^{1}S	Cl$^-$	461.5214	459.5769	459.6778	0.1009	1.844
$3s^2 3p^5$	^{2}P	Cl	461.3872	459.4821	459.5847	0.1026	1.802
$3s^2 3p^4$	^{3}P	Cl$^+$	460.9105	459.0486	459.1470	0.0984	1.763
	^{1}D		460.8589	458.9845	459.0867	0.1022	1.772
	^{1}S		460.7850	458.8892	458.9719	0.0827	1.813
$3s^2 3p^3$	^{4}S	Cl^{2+}	460.0369	458.2265	458.3067	0.0802	1.730
	^{2}D		459.9544	458.1227	458.2176	0.0949	1.737
	^{2}P		459.9007	458.0543	458.1334	0.0791	1.767
$3s^2 3p^2$	^{3}P	Cl^{3+}	458.4328	456.7889	456.8618	0.0729	1.571
	^{1}D		458.5184	456.7160	456.7916	0.0756	1.727
	^{1}S		458.5770	456.6082	456.6573	0.0491	1.920
$3s^2 3p$	^{2}P		456.6117	454.8616	454.9080	0.0464	1.704
$3s^2$	^{1}S		454.1239	452.4098	452.4677	0.0579	1.656
$3s3p^6$	^{2}S	Cl	460.978$^{\mathrm{a}}$	458.9168	459.0231$^{\mathrm{a}}$	0.1063	1.954
$3s3p^5$	^{3}P	Cl$^+$	460.4851$^{\mathrm{a}}$	458.5227	458.6132$^{\mathrm{a}}$	0.0905	1.872
	^{1}P		460.205$^{\mathrm{a}}$	458.2746	458.2893$^{\mathrm{a}}$	0.0147	1.916
$3s3p^4$	^{4}P	Cl^{2+}	459.5863	457.7479	457.8620	0.1141	1.724
	^{2}D		—				(1.84)
	^{2}P		—				(1.96)
	^{2}S		—				(1.72)
KL $3s3p^3$	^{5}S	Cl^{3+}	458.2849	456.5503	456.5771	0.0268	1.708
	^{3}D		458.1126	456.3005	456.4183	0.1178	1.694
	^{3}P		458.0331	456.2278	456.3332	0.1054	1.700
	^{3}S		457.8306	455.9975	456.1109	0.1134	1.720
	^{1}D		457.9918$^{\mathrm{a}}$	456.0259	456.1131$^{\mathrm{a}}$	0.0872	(1.72)
	^{1}P		457.8214	455.9543	456.0849	0.1306	1.736
$3s3p^2$	^{2}P	Cl^{4+}	455.8937	454.1190	454.2096	0.0906	1.684
	^{4}P		456.2204	454.5497	454.5668	0.0171	1.654
	^{2}D		456.1001	454.3284	454.4312	0.1028	1.669
	^{2}S		455.9481	454.2149	454.2651	0.0502	1.683
$3s3p$	^{3}P	Cl^{5+}	453.6715	452.0207	452.0289	0.0082	1.643
	^{1}P		453.4452	451.7239	451.7852	0.0613	1.660
$3s$	^{2}S	Cl^{6+}	450.5580	448.9302	—	0.0000	1.628
$3s^0$	^{1}S	Cl^{7+}	446.3614	444.7644	—	0.0000	1.597

[a] See text (Sect. 5.3.3)

Inversing Eqs. (4a) and (4b) and making a Löwdin orthonormalization[3] we obtain:

$$\Phi(\gamma_1\,{}^2\mathrm{S}) = 0.819514\Psi(\Gamma_1\,{}^2\mathrm{S}) + 0.573059\Psi(\Gamma_2\,{}^2\mathrm{S})$$

$$\Phi(\gamma_2\,{}^2\mathrm{S}) = 0.573059\Psi(\Gamma_1\,{}^2\mathrm{S}) - 0.819514\Psi(\Gamma_2\,{}^2\mathrm{S})$$

and finally the requested energies

$$E(\gamma_1\,{}^2\mathrm{S}) = -459.0231\ \text{a.u.}$$

$$E(\gamma_2\,{}^2\mathrm{S}) = -458.8654\ \text{a.u.}$$

---

[3] This orthonormalization is imposed by the neglect of the 4 remaining CSF's

so that the approximate internal correlation energy of the $\Phi(\gamma_1\,{}^2S)$ state is

$$E(\gamma_1\,{}^2S) - E_{HF}(\gamma_1\,{}^2S) = -459.0231 + 458.9168 = -0.1063 \text{ a.u.}$$

The calculation of the internal correlation energy of three other states, KL $3s3p^3({}^1D)$, KL $3s3p^5({}^3P)$ and KL $3s3p^5({}^1P)$ also exhibited strong interactions between CSF's.

In the first two cases we proceeded in the same way as we had done for the KL $3s3p^6({}^2S)$ state. Unfortunately, in the third case, the MCHF calculation did not converge and so we had to resolve the problem by means of a CI calculation performed with the orbitals of a E_{AV} calculation of the three interacting CSF's.

5.3.4. Atomic exact non-relativistic energies and error energies

For the chlorine atom (Z = 17) and its ions considered here (N = 18 to 14), no values for exact non-relativistic energies (E_{EX}^{NR}) are available since the tables of Scherr et al. [24] (SSM) are limited to Z = 20 and N = 10. Consequently, we tried to obtain such values through the relation

$$E_{EX}^{NR} = E_{EX} - E_{REL} \tag{5}$$

using the recent experimental energies (E_{EX}) of Bashkin and Stoner [25] and evaluating the relativistic energies (E_{REL}) by

$$E_{REL} \simeq E_{cHF} - E_{HF} \tag{6}$$

E_{cHF}[4] being the total (relativistic) energies of Fraga et al. [26]. Afterwards, using the internal correlation energy values (E_{CORR}^{I}) of Verhaegen and Moser [27a], we calculated, as a test, the non-internal correlation energies (E_{CORR}^{NI}) for the $C({}^3P)$ isoelectronic series according to the relation

$$E_{CORR}^{NI} = E_{EX}^{NR} - E_{HF} - E_{CORR}^{I}. \tag{7}$$

As can be seen from Table 7, those E_{CORR}^{NI} values ($E_{CORR}^{NI}(1)$), even approximately corrected for lamb-shift (LS) ($E_{CORR}^{NI}(2)$), exhibit an incorrect behavior as Z increases i.e. decrease for large Z instead of reaching a constant value.

Oppositely, the E_{CORR}^{NI} values ($E_{CORR}^{NI}(3)$) used previously [27] and based on the SSM E_{EX}^{NR} values exhibit a correct Z-dependancy, even for $Z \geq 10$. It seems thus that the experimental fitting performed by SSM to obtain E_{EX}^{NR} values is more appropriate than the direct *ab initio* determination of the relativistic contributions (relations (5) and (6)).

In order to avoid the difficulty of calculating reliable total relativistic corrections and hence reliable E_{EX}^{NR} values, we propose to transfer in the molecule not only the atomic non-internal correlation energies but also the atomic experimental relativistic energies leading (see Fig. 2) to the definition of a new concept, the *error energy* (E_E)

$$E_E = E_{CORR}^{NI} + E_{REL} = E_{EX} - E_{MCHF} \tag{8}$$

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[4] "cHF" stands for "corrected Hartree-Fock"

Table 7. Z dependence of non-internal correlation energy for $C(^3P)$ isoelectronic sequence (a.u.)

$1s^22s^22p^2(^3P)$	Z	$-E_{EX}$	$-E_{cHF}$	LS[a]	$-E^{I}_{CORR}$	$-E^{NI}_{CORR}(1)$	$-E^{NI}_{CORR}(2)$	$-E^{NI}_{CORR}(3)$
C^{I}	6	37.8574	37.7007	0.0014	0.0173	0.1394	0.1408	0.139
N^{II}	7	54.0795	53.9138	0.0025	0.0216	0.1441	0.1466	0.145
O^{III}	8	73.3204	73.1485	0.0040	0.0253	0.1466	0.1506	0.149
F^{IV}	9	95.5771	95.4023	0.0060	0.0287	0.1461	0.1521	0.153
Ne^{V}	10	120.8517	120.6763	0.0086	0.0320	0.1434	0.1520	0.156
Mg^{VII}	12	180.4658	180.2965	0.0158	0.0385	0.1308	0.1466	0.161
Si^{IX}	14	252.1969	252.0423	0.0259	0.0448	0.1098	0.1357	0.165
P^{X}	15	292.6218	292.4757	0.0321	0.0481	0.0980	0.1301	0.166

[a] Approximate lamb shift values [27]

which can be easily evaluated provided that E_{EX} values are available. The underlying hypothesis is that relativistic energies are transferable for $Z < 20$ which is a reasonable hypothesis [10a]. The establishment of E_E tables according to relation (8) will be discussed in the next section. Finally, in Table 8 we compare the contribution of E^{NI}_{CORR} and E_E to the dissociation of some molecules containing second row atoms. The perfect agreement observed shows the consistency of the new semi-empirical data tables (E_E) with those used up till now (E^{NI}_{CORR}).

Fig. 3 gives a complementary illustration of this consistency by showing the quite parallel variation of error and non-internal correlation energies, calculated at a fixed value $Z = 10$, as a function of the electron number. This parallelism shows also clearly that the relativistic contributions E_{REL} are independent of the occupation number of the $2p$ electrons and only slightly dependent on the number of $2s$ electrons (see the variation from 2 to 4 electrons in the figure) and the reason why therefore the transferability of the relativistic contributions is plausible. The

Table 8. Comparison of E^{NI}_{CORR} and E_E contribution to the dissociation energy of some molecules containing second row atoms (eV)

Dissociation process	ΔE^{NI}_{CORR}	ΔE_E
$H_2 \rightarrow 2H$	0.53	0.54
$N_2 \rightarrow 2N$	1.19	1.17
$O_2 \rightarrow 2O$	0.35	0.36
$F_2 \rightarrow 2F$	0.13	0.10
$H_2O \rightarrow H_2 + O$	0.66	0.66
$NO \rightarrow N + O$	0.795	0.78
$CO \rightarrow C + O$	0.84	0.85
$C_2 \rightarrow 2C$	0.74	0.75
$CO_2 \rightarrow CO + O$	0.585	0.58
$CN \rightarrow C + N$	1.15	1.14
$CO_2 \rightarrow C + 2O$	1.43	1.43
$H_2O \rightarrow O + 2H$	1.19	1.20
$HCN \rightarrow H + CN$	0.87	0.89
$HCN \rightarrow H + C + N$	2.02	2.03

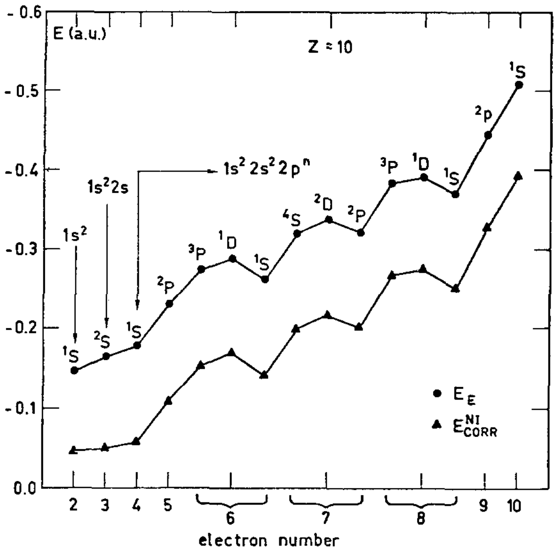

Fig. 3. Variation of non-internal correlation energies and error energies as a function of electron number (at Z = 10)

Z = 10 value has been chosen for that illustration as the greatest Z value for which the 2*s* and 2*p* electrons are effective valence electrons. Obviously the same parallelism is not observed for larger values of Z as a consequence of the importance of the relativistic effects of the inner shells in the corresponding atoms. However, such cases are not encountered within the chemical applications area we usually consider.

5.3.5. New atomic semi-empirical data tables

Error energy (E_E) tables were constructed according to relation (8) (Sect. 5.3.4) where E_{EX} for a LS state arising from a configuration Γ with N electrons was explicitly calculated as

$$E_{EX}(\Gamma LS, N) = -\sum_{n=1}^{N} I(\Gamma' L' S' J'_{\text{ground}}; n) + \frac{\sum_{J} (2J+1) T_e(\Gamma LSJ; N)}{\sum_{J} (2J+1)}$$

where the ionization potentials (I) of the lower J′ state of the Γ′ configuration with *n* electrons and the terms (T_e) of the J states were taken from Bashkin and Stoner (BS) Grotian diagrams [25].

i) *Second row atoms.* Results of E_E are presented in Tables 9, 10 and 11 for all states arising from the configurations $1s^2 2s^n 2p^m$ ($n = 0, 1, 2$; $m = 0$ to 6). Several values (indicated in parentheses) were extrapolated or interpolated due to the lack of experimental data. As a consequence, the use of E_E values derived above

Table 9. Error energies for states arising from $1s^2 2s^2 2p^n$ configurations (a.u.) ( ): Interpolated or extrapolated value

Z	Be(^{1}S)	B(^{2}P)	C(^{3}P)	C(^{1}D)	C(^{1}S)	N(^{4}S)	N(^{2}D)	N(^{2}P)	O(^{3}P)	O(^{1}D)	O(^{1}S)	F(^{2}P)	Ne(^{1}S)
4	0.052												
5	0.058	0.099											
6	0.067	0.110	0.151	0.163	0.149	(0.198)	(0.215)	(0.209)	(0.266)	(0.271)	(0.263)	(0.332)	(0.402)
7	0.080	0.126	0.170	0.181	0.161	0.213	0.230	0.220	(0.281)	(0.287)	(0.274)	(0.346)	(0.415)
8	0.102	0.150	0.195	0.207	0.184	0.239	0.256	0.243	0.303	0.311	0.294	(0.367)	(0.434)
9	0.133	0.183	0.229	0.241	0.215	0.275	0.292	0.276	0.336	0.345	0.324	0.399	(0.464)
10	0.179	0.230	0.276	0.288	0.261	0.320	0.339	0.322	0.383	0.392	0.368	0.443	0.507
11	0.242	0.296	0.342	0.355	0.326	0.385	0.402	0.384	0.449	0.458	0.433	0.508	0.569
12	0.323	0.380	0.428	0.440	0.410	0.469	0.487	0.468	0.534	0.543	0.516	0.592	0.650
13	0.430	0.492	0.542	0.554	0.523	0.582	0.602	0.582	0.647	0.656	0.627	0.702	0.759
14	0.568	0.635	0.690	0.701	0.668	0.730	0.758	0.734	0.794	0.803	0.772	0.845	0.903
15	0.740	0.816	0.878	0.888	0.855	0.919	0.951	0.924	0.981	0.988	0.955	1.028	1.086
16			(1.195)			1.155	1.175	1.146	1.212	1.219	1.183	1.254	1.314
17			(1.488)			1.448	1.458	1.419	1.498	1.512	1.479	1.536	1.597

allows us to estimate some missing term energies in BS's tables. It should be pointed out that the error limits on these estimations depend only on the quality of the E_{E} extrapolation so that for high term values, the relative uncertainty is very small (<0.05%). The results for estimated terms are presented in Table 12 and compared with those from Verhaegen and Moser (VM) [27a] proceeding from similar extrapolations of $E^{\mathrm{NI}}_{\mathrm{CORR}}$ values; most of the time a nice agreement is observed between both results.

Moreover, the term energies for the states $1s^22p^4\,{}^1\mathrm{D}$ (at Z = 11) and ${}^1\mathrm{S}$ (at Z = 14) presented here as well as those previously estimated by VM are in complete disagreement with BS's values. This disagreement could result from an incorrect assignment of the spectroscopic states in BS's tables.

Table 10. Error energies for states arising from $1s^22s2p^n$ configurations (a.u.) ( ): Interpolated or extrapolated value

Z	Li(^{2}S)	Be(^{3}P)	Be(^{1}P)	B(^{4}P)	B(^{2}D)	B(^{2}S)	B(^{2}P)	C(^{5}S)	C(^{3}D)	C(^{3}P)
3	0.046									
4	0.049	0.058	0.081							
5	0.054	0.064	0.107	0.078	0.130	0.122	0.150			
6	0.062	0.073	0.120	0.087	0.139	0.139	0.159	0.105	0.171	0.177
7	0.074	0.087	0.136	0.101	0.154	0.149	0.176	0.121	0.186	0.187
8	0.094	0.107	0.157	0.122	0.176	0.170	0.199	0.141	0.208	0.208
9	0.123	0.137	0.189	0.154	0.208	0.201	0.232	0.172	0.240	0.238
10	0.164	0.180	0.232	0.198	0.253	0.245	0.277	0.214	0.284	0.281
11	0.222	0.239	0.292	0.263	0.315	0.307	0.339	0.275	0.346	0.343
12	0.299	0.317	0.368	0.335	0.393	0.386	0.418	0.355	0.426	0.422
13	0.399	0.418	0.470	0.439	0.499	0.493	0.523	0.466	0.534	0.529
14	0.527	0.549	0.599	0.574	0.634	0.627	0.658	0.605	0.673	0.667
15	0.687	0.708	0.760	0.746	0.802	0.799	0.829	0.786	0.851	0.843
16	0.886									
17	1.127									

Z	C(^{3}S)	C(^{1}D)	C(^{1}P)	N(^{4}P)	N(^{2}D)	N(^{2}S)	N(^{2}P)	O(^{3}P)	O(^{1}P)	F(^{2}S)
3										
4										
5										
6	0.233	0.242	0.196	(0.218)	(0.266)	(0.278)	(0.305)	(0.329)	(0.355)	(0.456)
7	0.221	0.244	0.219	(0.227)	(0.277)	(0.284)	(0.314)	(0.337)	(0.368)	(0.463)
8	0.244	0.264	0.257	0.246	0.298	0.297	0.332	0.354	(0.391)	(0.479)
9	0.276	0.295	0.287	0.276	0.328	0.322	0.361	0.383	0.424	0.504
10	0.321	0.339	0.331	0.317	0.371	0.363	0.400	0.423	0.483	0.538
11	0.384	0.402	0.394	0.377	0.429	0.421	0.458	0.484	0.541	0.594
12	0.465	0.482	0.473	0.451	0.508	0.499	0.537	0.563	0.619	0.670
13	0.572	0.589	0.581	0.561	0.615	0.606	0.644	0.669	0.725	0.772
14	0.711	0.727	0.718	0.700	0.762	0.754	0.790	0.806	0.862	0.906
15	0.890	0.904	0.893	0.878	0.942	0.939	0.970	0.981	1.036	1.078
16				1.100	1.152	1.144	1.178	1.199	1.254	1.291
17				1.374	1.417	1.410	1.440	1.469	1.539	1.556

Table 11. Error energies for states arising from $1s^22p^n$ configurations (a.u.) ( ): Interpolated or extrapolated value

Z	He(^{1}S)	Li(^{2}P)	Be(^{3}P)	Be(^{1}D)	Be(^{1}S)	B(^{4}S)	B(^{2}D)	B(^{2}P)	C(^{3}P)	C(^{1}D)	C(^{1}S)	N(^{2}P)	O(^{1}S)
1	0.040												
2	0.042												
3	0.044	0.046											
4	0.046	0.050	0.061	0.107	0.132								
5	0.050	0.056	0.069	0.108	0.132	0.089	(0.156)	(0.177)					
6	0.056	0.064	0.078	0.117	0.135	0.100	0.163	0.187	(0.225)	(0.259)	(0.271)	(0.363)	(0.477)
7	0.067	0.076	0.092	0.130	0.149	0.115	0.175	0.187	(0.237)	(0.271)	(0.284)	(0.370)	(0.490)
8	0.085	0.094	0.111	0.149	0.169	0.136	0.194	0.207	0.256	0.290	0.303	(0.384)	(0.509)
9	0.110	0.122	0.140	0.178	0.198	0.166	0.224	0.236	0.283	0.319	0.331	0.407	(0.537)
10	0.147	0.160	0.180	(0.218)	(0.238)	0.207	0.265	0.277	0.323	(0.359)	(0.371)	0.442	
11	0.198	0.214	0.236	0.274	0.295	0.269	0.323	0.335	0.381	(0.417)	0.429	0.497	
12	0.265	0.285	0.307	0.346	0.367	0.336	0.397	0.410	0.456	0.492	0.504	0.570	
13	0.353	0.379	0.403	0.443	0.463	0.433	0.497	0.508	0.556	0.592	0.604	0.670	
14	0.465	0.497	0.525	0.567	0.586	0.560	0.626	0.643	0.687	0.721	(0.733)	0.808	
15	0.606	0.646	0.673	0.708	0.725	0.721	0.797	0.820	(0.860)	(0.894)	(0.906)	1.000	
16	0.779											1.174	
17	0.990												

ii) *Chlorine atom.* The E_{E} values for chlorine atom presented in Table 6 were obtained exactly in the same way as those for second row atoms. However, several remarks should be made concerning this Table.

First, for the configurations KL $3p^n (n = 1$ to $6)$ no experimental energies are available in BS's tables. Since we did not, up till now, systematically calculate E_{E} values for KL $3s^n 3p^m$ configurations at various Z values, no extrapolation or interpolation is possible. Consequently the corresponding E_{E} values were set to zero in the molecular calculations. In fact their contributions to the molecular error energy are expected to be negligible, their weights in the decomposition of the zeroth-order wavefunction being very small (for instance $\ll 10^{-6}$ for ClO). Secondly, for the states ^{2}D, ^{2}P, ^{2}S arising from the configuration KL $3s3p^4$ no experimental energies are available either. Consequently, the E_{E} values were estimated with respect to the corresponding E_{E} values in Argon (Z = 18).

Finally for the KL $3s3p^3(^1\mathrm{D})$, KL $3s3p^5(^1\mathrm{P}, ^3\mathrm{P})$ and KL $3s3p^6(^2\mathrm{S})$ states which are in fact far from being pure states, transformations using MC coefficients

Table 12. Addenda to Bashkin and Stoner tables

Z	Conf.	State	T_e (cm^{-1})[a] this work	T_e (cm^{-1})[a] VM	T_e (cm^{-1}) BS
5	$1s^2 2p^3$	^{2}D	(97500)	(97350)	
		^{2}P	(109500)	(105440)	
6	$1s^2 2p^4$	^{3}P	(154700)	(155170)	
		^{1}D	(159500)	(159740)	
		^{1}S	(184800)	(185420)	
7	$1s^2 2p^4$	^{3}P	(219400)	(219820)	
		^{1}D	(229100)	(229280)	
		^{1}S	(264400)	(265270)	
	$1s^2 2p^3$	^{2}P	(232000)	(235380)	
	$1s^2 2s 2p^4$	^{4}P	(87500)		
		^{2}D	(121400)	(120880)	
		^{2}S	(141900)	(159840)	
		^{2}P	(157200)	(157090)	
8	$1s^2 2p^5$	^{2}P	(316600)	(318530)	
	$1s^2 2s 2p^6$	^{1}P	(183500)		
10	$1s^2 2p^2$	^{1}D	317700 ± 200	317600 ± 200	
		^{1}S	393300 ± 200	392800 ± 200	
	$1s^2 2p^4$	^{1}D	436600 ± 200	436600 ± 300	
		^{1}S	500500 ± 200	501000 ± 300	
11	$1s^2 2p^4$	^{1}D	506200 ± 200	506200 ± 400	539430
14	$1s^2 2p^4$	^{1}S	819800 ± 200	818100 ± 900	669562
15	$1s^2 2p^4$	^{3}P	743900 ± 400	742700 ± 700	
		^{1}D	791200 ± 400	789100 ± 900	
		^{1}S	900500 ± 600	898800 ± 1100	

[a] Terms indicated in parentheses are "uncertain" as a consequence of the delicate extrapolations performed at low Z values (see Ref. [27a])

discussed in Sect. 5.3.3 were used to connect the experimental energies, $E_{EX}(\Psi)$, to the monoconfigurational energies $E_{EX}(\Phi)$ used to calculate E_E.

6. Conclusion

In this work, we have presented an extension of an economical method of calculation of the molecular correlation energy, developed in previous work. The extension concerns the applicability of the method to third row atoms and an analysis of its consequences at the three levels of energy partition, i.e. the zeroth-order energy, the internal and the non-internal correlation energies. The particular points that have been investigated are: the optimization of polarization and correlation $3d$ orbitals, the influence of these $3d$ orbitals on the "atoms-in-molecule" expansion of the zeroth-order wavefunction and the determination of the required atomic semi-empirical data together with the definition of the new concept: the error energy. Direct semi-empirical tables of error energies were determined without having to introduce the artefact of an approximate extraction of the relativistic contributions from the experimental energies.

In this paper, the chlorine atom has been chosen as a test for the above methodological advances. Molecular applications devoted to the ClO, HCl, HCl^+ and NCl molecules are presented in a second paper, in which it is shown that the economical features and the reliability of the method are preserved. However, all the conclusions presented here may be extended to any other third row atom so that many applications to molecules containing any third row atom may be expected in the near future.

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