

Contracted and Uncontracted Oscillator Orbitals in CI Calculations on Two Electron Systems

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Oscillator orbitals as expansion functions for the correlation holes have been checked by using them in two simple two electron systems, H_2 and Li^+ .

A contraction of the oscillators has been introduced and proved useful to ameliorate energy and convergence rate.

Oszillatororbitale als Entwicklungsfunktion zur Darstellung des Korrelationsloches werden durch Anwendung bei zwei einfachen Zweielektronensystemen H_2 und Li^+ geprüft. Eine Kontraktion der Oszillatoren wird eingeführt, welche die Energie und die Konvergenzgeschwindigkeit verbessert.

Essai d'orbitales oscillantes comme fonctions de base pour les trous de corrélation dans deux systèmes biélectroniques simples: H_2 et Li^+ .

L'introduction d'une contraction des ces orbitales s'est avérée utile pour améliorer l'énergie et la vitesse de convergence.

1. Introduction

Several considerations support the convenience of using in MO–CI calculations a basis of localized orbitals (LO) rather than delocalized one.

Suffice it to recall here that the heuristic value of the CI calculations is actually greatly emphasized because one is allowed to get a quantum-mechanical counterpart (electronic correlation included) of the intuitive “chemical” model of the bonding, which possibly might take into account the bond transferability, the inductive effect along the bonds, the short range forces arising from localized (e.g. reactive) perturbations, etc. The final goal of such a type of calculations should presently be to get semiempirical recipes to be used on molecular systems of large dimensions.

The first step in this direction is to define a suitable set of localized virtual orbitals, connected with SCF LO's which can be obtained from the canonical ones by means of an appropriate orthogonal transformation.

The pioneer work in this field is due, as far as we know, to Foster and Boys [1]: they introduced a new type of localized orbitals (exclusive orbitals) of fairly simple determination and defined, for each LO, a set of virtual localized orbitals (oscillator orbitals) with a view to building up additional Slater determinants for the CI process. This sort of virtual orbitals has however some deficiencies; the actual calculations made in the original paper [1] (on the formaldehyde molecule) are too limited to evidence them, therefore, as a matter of convenience, we will make reference to later results of our Laboratory [2] related to a type of virtual orbitals somewhat different from Foster and Boys's, both of them having

however the characterizing feature of being obtained through an orthogonal transformation from the set of virtual SCF MO's. The results of Ref. [2] show that it was not possible to obtain, for each exclusive orbital, more than two or three satisfactory virtual LO's, the other ones being completely delocalized and ineffective as regards the corresponding energy improvement. This is a consequence of the well known fact that the virtual SCF orbitals are not suitable to expand the correlation hole in the regions of higher electron density. Such an inconvenience is not overcome by enlarging the basis set; computational problems and storage facilities of the computer quickly become the limiting factors.

Another proposal made by Boys aims to avoiding this inconvenience [3]. For each SCF LO a set of adjustment functions is defined; these functions, after a suitable orthonormalization process, performed in two stages, become the oscillator orbitals. These adjustment functions are not defined in terms of the virtual SCF orbitals, but directly originate in the SCF LO's according to a genealogical procedure. This is the peculiar feature of the oscillator orbitals (new version); this paper is devoted to a control of how such a set works.

2. Definition of Oscillator Orbitals and Some Results for the H_2 Molecule

Let us suppose to have, for a given molecule, a set of LO's obtained from a previous SCF calculation. Let us pick up one among them, φ_a , which describes, for example, a bond between the atoms A and B. The correlation between the electron pair belonging to this bond may be described, in a first approximation, by including the configurations arising from substitutions of φ_a with polarized orbitals which cause the electrons to avoid each other, like $\varphi_a x_c$, $\varphi_a y_c$, $\varphi_a z_c$. The subscript c emphasizes that the most suitable origin of the polarization function lies in the charge center of the distribution $\varphi_a^* \varphi_a$ with axes parallel to the principal axes of the inertia tensor of such a charge distribution.

This statement is intuitively acceptable because such a procedure corresponds to expand at first the most important part of the correlation hole. An empirical verification may be found e.g. in Ref. [2].

Boys [3] extends this idea and defines accordingly a system of adjustment functions:

$$\bar{\varphi}_{apqs} = \varphi_a x_c^p y_c^q z_c^s .$$

From them one can obtain the oscillator orbitals φ_{apqs} , after a suitable orthonormalization process (see Ref. [3] for a detailed description) which preserves any symmetry present among the φ_{apqs} , maximizes the overlap between the oscillator orbital and the original adjustment function and retains $\varphi_{a000} = \varphi_a$. The virtual SCF space is therefore completely discarded. The adjustment functions are sufficiently general (no limitations are imposed on the integers p, q, s) to consider the set as complete.

The practical use of the oscillator orbitals requires a systematization of the computing machinery going beyond the limits of a simple investigation as the present one. It may be recalled here that a promising suggestion was made by Boys himself in another paper [4]. The numerical results reported in this paper were obtained by means of an exact expansion of the oscillator orbitals into Slater-type atomic orbitals (STO's).

Table 1. *Some results for H₂ molecule^a*

SCF wavefunction				Oscillator orbital CI wavefunction	
Center	STO	ζ	Coeff.	Orbital	Coeff.
1	1s	1.14	0.58685	φ_a	0.99332
1	$2p_\sigma$	1.77	0.03196	$\varphi_a z_c$	-0.09206
2	1s	1.83	-0.01777	$\varphi_a x_c$	-0.04914
2	2s	1.83	-0.02673	$\varphi_a y_c$	-0.04914
2	$2p_\sigma$	1.83	0.00000		
2	3s	1.83	-0.06351		
3	1s	1.14	0.58685		
3	$2p_\sigma$	1.77	-0.03196		
Energy: -1.13345				Energy: -1.15061	
Geometry					
Center	x	y	z		
1	0.0	0.0	-0.7004		
2	0.0	0.0	0.0		
3	0.0	0.0	0.7004		

^a Energies and distances in a. u.

A first test has been performed on the hydrogen molecule, using as a starting point a good SCF wavefunction [5] whose basis set is characterized by having STO's centered also on the molecular midpoint (see Table 1). The corresponding SCF energy (-1.13345 a.u.) is sufficiently near the Hartree-Fock limit (the latter being -1.133629 a.u.) to consider any further energy improvement as being due to correlation. Inclusion of the first three oscillator orbitals, having all $p + q + s = 1$, in the CI process leads to an energy of -1.15061 a.u., with an improvement over the SCF value of -0.01716 a.u., corresponding to 41% of the correlation energy.

The SCF basis set being quite extended, it is obvious to forecast that the conventional CI method works in this case as much as possible. In fact, if one uses the SCF basis set implemented by some π virtual orbitals (STO's $2p_x$ and $2p_y$ having the same orbital exponent as the $2p_z$ STO's already present in the set) one obtains $E = 1.17102$ a.u., i.e. $\cong 92\%$ of the correlation energy. Confining ourselves to the three best configurations ($1\sigma_u$, 1π and $1\bar{\pi}$) we get a total energy of -1.15945 a.u., which corresponds to an energy improvement over the SCF value of -0.026002 a.u., (64% of the correlation energy) decidedly better than that obtained using oscillator orbitals.

A closer analysis shows that the main differences are in the σ part. In fact a CI calculation with the first excited σ configuration leads to $\Delta E = -0.015748$ a.u. and the corresponding one with $\varphi_a z_c$ leads to $\Delta E = -0.010077$, whereas the conventional method with configurations $1\pi_u^2$ and $1\bar{\pi}_u^2$ leads to $\Delta E = -0.011287$ a.u., to be compared with $\Delta E = -0.007663$ obtained with $\varphi_a x_c$ and $\varphi_a y_c$.

For other comparisons the reader is deferred to other CI results available in the literature, e.g. to the paper of Weiss, McLean and Yoshimine [6].

Such comparisons may result more favourable to the oscillator orbitals than the present ones, but we are here especially interested in pointing out that even the oscillator orbitals show some deficiencies in the expansion of the correlation. The main reason for such a poor behaviour seems to lie in the fact that the multiplication of the localized orbital by positive powers of the coordinates, though giving the correct shape to the adjustment functions, excessively spreads out the charge distribution. The fact may be easily verified in the preceding example if one compares the spatial density distribution of the σ_u natural orbital with that arising from the φ_{azc} function.

It would be of some interest to look for a correction in this sense to all the oscillator orbitals. The simplest way to obtain it is the introduction in the oscillator orbitals of a sort of contracting factor.

In the next section are reported some results obtained with an exponential contraction factor.

3. Contracted Oscillator Orbitals

For the contraction factor we have tentatively adopted the form $\exp(-kr_c)$, with k positive, r_c being the distance from the orbital charge center.

Such a choice was suggested by practical reasons: budget restrictions have not allowed us to extend the calculations on polycentric systems to oscillators having a degree (i.e. sum of the exponents p, q, s) higher than one, which are necessary to test how a contraction factor works. As a consequence we considered the simpler case of an atomic system, and in this case the form chosen is the most suitable for expanding oscillator orbitals in terms of STO's.

When one deals with a monocentric system, it is convenient to re-state the adjustment functions in spherical coordinates. The expression:

$$\bar{\psi}_{antmk} = \varphi_a r_c^n Y_l^m(\vartheta, \varphi) \exp(-kr_c),$$

where $Y_l^m(\vartheta, \varphi)$ is a real spherical harmonic, has the advantage of taking directly into account the radial correlation. Terms like $\bar{\psi}_{an000}$ do not actually appear in the original definition. Of course this definition contains also the older: for example $\bar{\psi}_{a1100} = \varphi_a r_c Y_1^0$ corresponds to $\bar{\varphi}_{a001} = \varphi_a z_c$, etc. The orthonormalization process (Boys' one may be conserved, with minor modifications) will lead to oscillators having the correct nodal surfaces.

For a numerical test we have chosen the Li^+ ion. The SCF wavefunction, reported in Table 2, was taken from an early work of our Laboratory [7] and the corresponding energy is, again, very close to the H-F limit (-7.2364135 a.u. [8]).

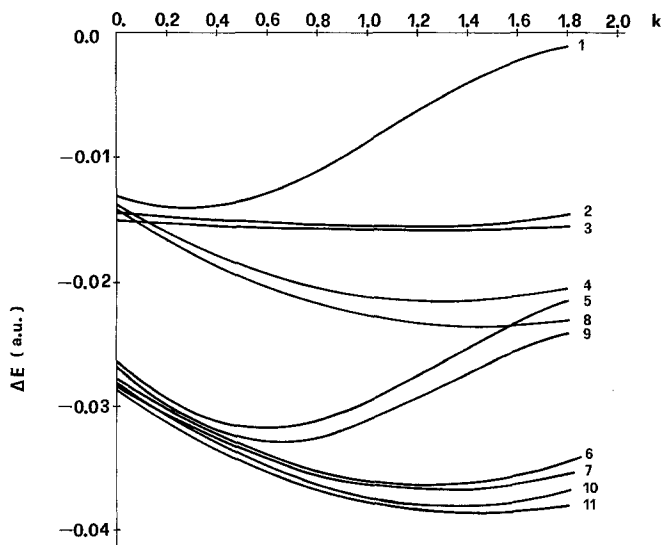
A first set of calculations was made without contraction factor ($k=0$). To evidence the convergence rate different cases are reported in Table 3. Column 2 reports the oscillator orbitals considered in each case, the notation should be evident: the symbols $3(2p)$ and $5(3d)$ respectively indicate the sets of three p -type oscillators φ_{a11m} and of five d -type oscillators φ_{a22m} . Column 3 reports the energy increment with respect to the SCF value, obtained by complete diagonalization of the corresponding secular matrix.

Table 2. SCF wavefunction for Li^+

Basis orbitals				Coefficients
n	l	m	ζ	
1	0	0	2.448	0.88935561
1	0	0	4.58	0.12546063
2	0	0	5.00	0.00011982
$E = -7.236412$				

Table 3. CI results for Li^+ with some sets of oscillator orbitals

Wave function	Oscillator set	Without contraction	With contraction	
		ΔE	k	ΔE
1	r	-0.013113	0.26	-0.01390
2	r, r^2	-0.014632	1.23	-0.01561
3	r, r^2, r^3	-0.015126	1.23	-0.01582
4	$3(2p)$	-0.013799	1.26	-0.02154
5	$r, 3(2p)$	-0.026449	0.6	-0.03170
6	$r, r^2, 3(2p)$	-0.027864	1.2	-0.03631
7	$r, r^2, r^3, 3(2p)$	-0.028432	1.4	-0.03652
8	$3(2p), 5(3d)$	-0.014212	1.5	-0.02344
9	$r, 3(2p), 5(3d)$	-0.026817	0.65	-0.03300
10	$r, r^2, 3(2p), 5(3d)$	-0.028235	1.34	-0.03833
11	$r, r^2, r^3, 3(2p), 5(3d)$	-0.028767	1.46	-0.03842

Fig. 1. ΔE dependence on the contraction factor k for all the Li^+ wavefunctions listed in Table 3

The first three wavefunctions contain only radial terms. Wavefunction 4 contains Boys' oscillators of the first degree and wavefunction 7 those of the first and second degree. Energies for wavefunctions 3, 7 and 11 are the approximations, within the set here employed, of the S, P and D limits for the Li^+ ion; a comparison with accurate results is performed in Table 4.

As a further step, in each of the wavefunctions of Table 3 a contraction factor was introduced, equal for all the oscillator orbitals included in the wavefunction. Results are graphically reported in Fig. 1. Each curve refers to a different wavefunction (the reference numbers are the same as in Table 3) and shows how energy changes when contraction factor increases. The optimal values of k and the corresponding energy improvements are reported in the last two columns of Table 3.

When only the first radial oscillator is included in the calculation, the optimum value of the contraction factor is low (wavefunction 1), whereas by enlarging the number of radial oscillators the wavefunction becomes more and more insensitive to the contraction factor (wavefunctions 2 and 3). Contraction factors for the first angular oscillators are larger than for radial oscillators (wavefunctions 4 and 8). The optimum k values for more complete wavefunctions are easily rationalized in comparison with the values of the simpler aforementioned cases. The energy improvement due to the contraction factor is sensible especially when a larger number of oscillators is employed.

Table 4. Comparison of energies for Li^+ (a.u.)

	Accurate results		This paper			
		% ^d	$k=0$	% ^d	k best	% ^d
HF	-7.236413 ^a	0	-7.236412	0	-7.236412	0
HF + S	-7.25242 ^b	37.3	-7.25153	35.2	-7.25221	36.8
HF + S + P	-7.27575 ^b	91.7	-7.26484	66.3	-7.27301	85.3
HF + S + P + D	-7.27845 ^b	98.0	-7.26512	66.9	-7.27481	89.5
Exper.	-7.2798 ^c		—		—	

^a Ref. [8].

^b Ref. [9].

^c Ref. [10].

^d % of the correlation energy (with allowance for relativistic energy).

A comparison with accurate results is made in Table 4. With three radial oscillators, 98% of the corresponding correlation energy is accounted for. Going to superior limits, 88% of the S + P correlation energy is reproduced and 74.5% of the S + P + D value. Such results are favourably compared with limited CI performed on large basis sets.

On wavefunction 6, which seems to us to be an acceptable compromise between accuracy and simplicity, the contraction factors of the radial oscillators and those of the angular ones were allowed to vary independently. As one could expect, on the basis of the results of Fig. 1, the new values do not noticeably

differ from the previous ones: $k(\text{rad})=1.1$ and $k(\text{ang})=1.3$. Also the energy does not change appreciably: 0.03640 against 0.03636 a.u.

The quite limited checks on oscillator orbitals here reported may give an answer only to a part of the question about the convenience of using oscillators in actual molecular calculations. The whole orthonormalization procedure for systems having more than two electrons must be checked carefully and appropriate integration techniques for calculating secular matrix elements are necessary. In any case the introduction of some sort of contraction factor, which at least for inner shells may be chosen equal for all the pertinent oscillators, can improve the energy and even the convergence rate.

Appendix

On Second Order CI Calculations

When one tries to improve a SCF wavefunction by means of a CI treatment, one is strongly exposed to the temptation of confining the calculation to the second order only. Two reasons may be alleged for: the calculations are far simpler, a quite limited number of the secular matrix elements being necessary, and the results are easily interpreted in terms of effects on a single SCF orbital. The goal mentioned in the introduction, to get semiempirical recipes useful to deal with large molecules, could be in this way facilitated.

The application of a perturbative treatment to an oscillator interaction problem requires some manipulations on the zeroth-order hamiltonian (see Ref. [11]). In fact the usual perturbative treatment is not possible because we have not expansion functions which are eigenfunctions with known eigenvector of H_0 . A way of circumventing this difficulty is to define a new unperturbed hamiltonian

$$H'_0 = H_{\text{HF}} + \sum_i \langle i|V|i\rangle |i\rangle \langle i|$$

and a new perturbation

$$V' = V - \sum_i \langle i|V|i\rangle |i\rangle \langle i|.$$

Here the set $|i\rangle$, formed by the oscillators together with the exclusive orbital $|0\rangle$, is considered orthonormal and complete; i.e.

$$\langle i|j\rangle = \delta_{ij}, \quad \sum_i |i\rangle \langle i| = 1.$$

With such a partition of the complete hamiltonian, the second order energy, in the Rayleigh-Schrödinger treatment is written as:

$$E^{(2)} = \sum_{i \neq 0} (\langle 0|H|0\rangle - \langle i|H|i\rangle)^{-1} \langle 0|V|i\rangle \langle i|V|0\rangle. \quad (1)$$

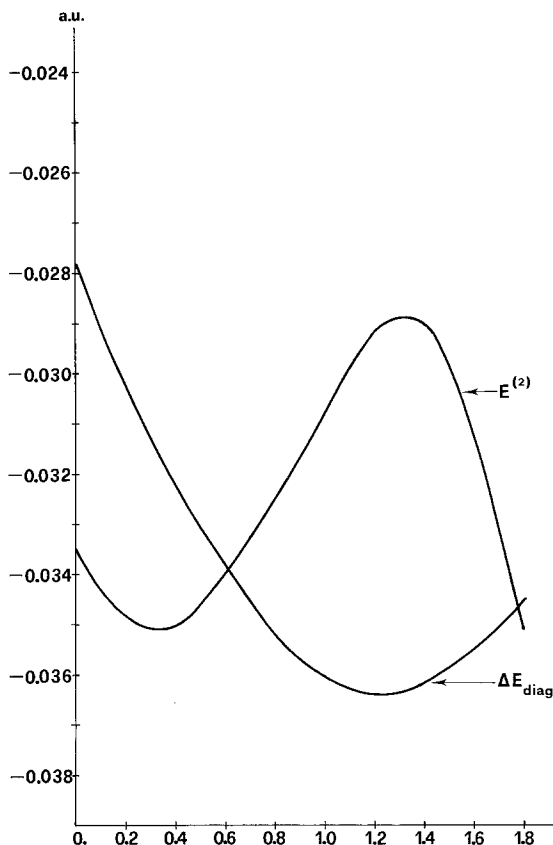


Fig. 2. Comparison of exact and second order energy improvement for wavefunction 6 of Table 3

Such an expression is frequently employed, even with the conventional virtual orbitals.

In this appendix we wish to point out, using a numerical example taken from the preceding calculations, that such a formula may give sometimes a very poor approximation. Fig. 2 reports the energy changes for wavefunction 6 of Li^+ varying the contraction factor calculated either exactly (curve ΔE_{diag} , the same as in Fig. 1) or according to Eq. (1). Similar trends have been found also for the other wavefunctions considered in Fig. 1.

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