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On the Direct Calculation of Localized HF Orbitals in Molecule Clusters, Layers and Solids

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It is shown that the computational effort involved in HF calculations can be considerably reduced by applying the following concepts: 1) the use of a localization operator for the direct determination of localized non-orthogonal HF orbitals, 2) the approximation of the interaction potential between different localization centres by a Hartree-like ansatz, 3) the successive calculation of many-body corrections to molecular properties such as the total energy. A numerical application to LiH layers and solid LiH is described.

Key words: Localized orbitals – Direct localization – Many-body expansion

1. Introduction

The main difficulty with the HF-Roothaan method is, as is generally known, the fact that when using *n* basis functions approximately $n^4/8$ two-electron integrals have to be calculated, stored and manipulated within the SCF iterations.

This difficulty can be overcome by departing from the conventional method which involves simultaneous calculation of all orbitals of a molecular system. The obvious alternative is to divide the system into subsystems each with a relatively small number of orbitals, and to treat these subsystems separately, each in the field of the others. However, this partitioning can only lead to a computational simplification, if it is coupled with a corresponding partitioning of the basis set. This is the case when different orbital groups belong to different symmetry species or – more importantly – when the orbitals are localized and different orbital groups belong to different localization centres.

The transformation from canonical HF orbitals to localized orbitals has been extensively studied in the past [1–6]. For most of these procedures it is necessary to know the canonical HF orbitals, and a reduction of the computational effort is not achieved. A direct calculation has been suggested by different authors [7–13], but has been performed in very few cases until now. Two points should be made here. Firstly, there is no marked saving of computer time, if the localized orbitals are mutually orthogonal: the so-called "orthogonalization tails" of a particular orbital would require additional basis functions belonging to neighbouring localization centres. Secondly, the use of localized orbitals brings a reduction from four-centre to three-centre terms in the Fock matrix, as pointed out by Gilbert and Kunz [14], but does not as such eliminate the four-centre terms in the expressions for molecular properties such as the total energy.

A simplification through the use of localized orbitals can therefore only be achieved with certain additional approximations. An obvious approximation pertains to the interaction between different subsystems; a further approximation considered by us deals with the representation of two-centre terms in the first-order density matrix. These approximations together with the procedure used by us for calculating the localized orbitals are discussed in Sect. 2. The results for the LiH layer and solid LiH are given in Sect. 3.

2. Method

The determination of localized orbitals is achieved by the addition of a localization operator of the form $\rho A \rho$ to the Fock operator [8]. Here ρ is the first-order density matrix and A a suitably chosen localization potential. The arbitrary nature of A should be taken advantage of to keep the additional effort for the calculation of $\rho A \rho$ to a minimum. The main problem here is that for non-orthogonal orbitals $|\alpha\rangle$, $|\beta\rangle$ ρ includes the inverse overlap matrix S^{-1}

$$\rho = \sum_{\alpha,\beta}^{\text{occ}} |\alpha\rangle\, S^{-1}_{\alpha\beta}\, \langle\beta| \tag{1}$$

For large clusters, and in particular for systems with translational symmetry such as layers and solids, the effort for the calculation of S^{-1} cannot be neglected, especially since $\rho A \rho$ has to be newly calculated for every step of the SCF iteration. We therefore adopt the following procedure. With

$$\rho = \rho_0 + (\rho - \rho_0) \tag{2}$$

(where ρ_0 is the "partial-density" matrix built up from the orbitals of the subsystem under consideration) we get

$$\begin{aligned} \rho A \rho = {} & \rho_0 A \rho_0 + \rho_0 A(\rho - \rho_0) \\ & + (\rho - \rho_0) A \rho_0 + (\rho - \rho_0) A (\rho - \rho_0) \end{aligned} \tag{3}$$

The first and fourth terms on the right-hand side can be ignored as they only bring about a transformation within the orbital group under consideration or within the complementary subspace. The second and third terms are the important ones, as they couple the orbitals under consideration with the orbitals localized at other centres. This statement is contrary to the work of Kunz [15, 16], who uses a localization operator of the form $\rho_0 A \rho_0$; the only possible effect of this operator is to reorder the eigenvalues. Retaining the second and third terms in (3) and introducing the approximation

$$\rho-\rho_0 \approx (1-\rho_0) \sum_j{}' \rho_j (1-\rho_0) \tag{4}$$

we obtain an expression which does not include S^{-1} but on the other hand is a valid localization operator in the sense that it operates on the HF manyfold only.

The localization potential used by us is

$$A=\sum_j{}' C_j \cdot \operatorname{erfc}\left(\sqrt{\varepsilon_j}\,|\boldsymbol{r}-\boldsymbol{r}_j|\right) \cdot |\boldsymbol{r}-\boldsymbol{r}_j|^{-1} \tag{5}$$

which can be interpreted as a superposition of screened repulsive Coulomb potentials surrounding the subsystem under consideration. The matrix elements of A have the same structure as those of the electron-nucleus potential.

In order to assess the influence of the localization operator on the results, we show in Fig. 1 for the LiH molecule the dependence of the total energy E on the parameter C_1 of the localization potential centred on Li. The experimental geometry was used and the basis set consisted of five s functions for both Li and H and one function in the bond midpoint (attributed to the H subsystem). Without localization the orbitals become too diffuse and the resulting energy is even higher than that of the isolated subsystems Li^+ and H^-. With increasing localization strength the energy asymptotically approaches a limit. This means that localization is necessary but not critical as long as it is sufficiently strong. This also means that methods which do not include localization (e.g. the MCF method of Ladik [17]) could run into difficulties for strong overlap of the subsystems.

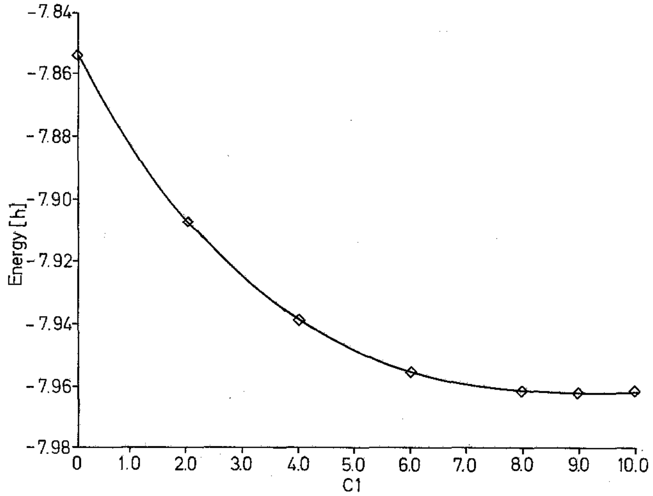

Fig. 1. Total energy E of the LiH molecule as a function of the parameter C_1 of the localization potential A_1 (cf. Eq. (5)) centred on Li. (The dependence of E on A_2, centred on H, is very weak.) The basis set b) of Table 5 was used

We now want to assess the computational effort involved in a HF calculation using non-orthogonal localized orbitals, and to introduce, step by step, approximations of the interaction between different orbital groups to reduce the effort even further. Let us, for simplicity, suppose that the molecular system includes M orbitals, which are partitioned into k subsystems each with m orbitals. Correspondingly, the N basis functions are taken as divided into k groups each with n functions. In a conventional HF-Roothaan calculation we have to evaluate $\sim N^4 = n^4k^4$ integrals. When using non-orthogonal localized orbitals we only need those Fock matrix elements between basis functions of the same subsystem and thus only $\sim n^4k^3$ integrals.

Owing to the spatial separation of the subsystems, the interactions within the molecular system can be classified as strong intra-group and comparatively weak inter-group interactions. Accordingly, for the intra-group interaction the Hartree-Fock expression should be used, whereas for the inter-group interaction an approximate potential such as a Hartree-type potential seems appropriate

$$\rho \approx \sum_j \rho_j \tag{6a}$$

$$\rho \approx \quad \rho_0 \tag{6b}$$

Here ρ_j is the partial-density matrix built up from the orbitals of localization centre j. (6a) is suitable for representing the Coulomb part of the HF potential; it is charge-conserving and exact in the limiting case of non-overlapping subsystems. (6b) can be applied in the exchange potential; the Fermi hole corresponds exactly to one electron in the approximation (which would not be the case if e.g. an additional X_α-potential were used for the inter-group exchange [17]).

These approximations lead to a reduction of the computational effort by a further factor k to $\sim n^4k^2$. The question still remains, however, what effect these field-approximations have on the calculated localized orbitals. As an example, we have calculated the $(FH)_2$ dimer using a (2,1/1) basis set; the Hartree-Fock total energy was -170.15196 [h]. Localizing the orbitals and using the above approximations in the iteration process yields orbitals which when inserted in the Hartree-Fock energy expression give -170.15143 [h]. The difference is negligible when one considers the computational saving.

A further simplification is possible in the following way: in (6a) one can insert

$$\begin{aligned}\sum_j{}' \rho_j &= \sum_j{}' \sum_{p,q} D_{p_j,q_j}\chi_{p_j}(r)\chi_{q_j}(r) \\ &\approx \sum_j{}' \sum_p C_{p_j}\chi^2_{p_j}(r)\end{aligned} \tag{7}$$

Here $D_{p_jq_j}$ is the first-order density matrix in the basis-function representation and χ_{p_j}, χ_{q_j} basis functions belonging to localization centre j. The C_{p_j} can be determined by a least-squares fit under the restriction of charge conservation. This approximation improves as the basis set becomes larger; it refers only to inter-group interaction and reduces the number of integrals necessary for this interaction to approximately $\sim n^3k^2$. As the integrals to be calculated for the isolated subsystems are

$\sim n^4 k$ in number, the intra-group effort is predominant for systems with $n > k$, and a further reduction of the inter-group effort is not worthwhile.

Two questions arise: 1) How can one in a simple way determine molecular properties such as the total energy from the non-orthogonal localized orbitals obtained in the SCF iteration? 2) Is it possible to successively improve on the above-mentioned approximations if required?

The following procedure for the total energy serves to illustrate our method as a whole. The first step is to calculate the total energy E_0 using a suitable approximation (to be dealt with below) for the first-order density matrix ρ. We then couple a pair i,j of neighbouring subsystems to a new, larger subsystem and repeat the calculation. (If one does not want to improve the orbitals, the SCF iteration does not have to be repeated.) The total energy $E_0(i,j)$ is now evaluated as in the first step, and we denote the difference $\Delta E_{ij} \equiv E_0(i,j) - E_0$ as the two-body correction for the subsystems i,j. In this way it is possible to determine all relevant two-body corrections ΔE_{ij} which are not equivalent by symmetry, and subsequently, if required, three-body corrections ΔE_{ijk}, and so on. Thus one gradually approaches the HF total energy which is an upper limit for the true total energy.

The method is only practicable if the number of non-negligible many-body corrections is small. The choice of the approximation for ρ, or more exactly, the approximation for S^{-1} in the expression (1) for ρ, proves to be crucial. Symmetrically orthogonalizing within each subsystem, and setting $S^{-1}_{\alpha\beta} = 0$ otherwise, we obtained slow convergence for solid LiH and even divergence of the many-body expansion for diamond. This is also illustrated in Table 1, where the HF energy for solid LiH is given for various stages of the Löwdin expansion of S^{-1}; with the minimal basis set the Löwdin expansion converges, but third-order terms are necessary to ensure accuracy to $5 \cdot 10^{-3}$ [h]; with the larger basis set the Löwdin expansion does not seem to converge at all.

The conclusion is that the exact S^{-1} should be taken for ρ, to obtain a practicable many-body expansion. As S^{-1} only has to be calculated once, little extra effort is involved. For clusters S^{-1} can be determined directly; for layers and solids we use an iterative process

$$(S^{-1})_{n+1} = (2 - (S^{-1})_n S) \cdot (S^{-1})_n \qquad (8)$$
$$(S^{-1})_0 = \lambda \cdot \mathbf{1}$$

For $\lambda = 1$ (8) is identical with the Löwdin expansion, the nth iteration step including

Table 1. Total energies E for solid LiH (NaCl structure, lattice constant $a = 3.803$ [b]) for various stages of the Löwdin expansion of S^{-1}. $\bar{S} \equiv \mathbf{1} - S$. a) and b) refer to basis sets α) and β) of Table 7

	a)	b)
$E(S^{-1} \approx 1)$	−6.7279 [h]	−8.1258 [h]
$E(S^{-1} \approx 1 + \bar{S})$	−6.6605	−7.9964
$E(S^{-1} \approx 1 + \bar{S} + \bar{S}^2 + \bar{S}^3)$	−6.6689	−7.9537
$E(S^{-1}$ exact$)$	−6.6719	−8.0328

Step of iteration	S_{11}^{-1}	S_{12}^{-1}	S_{22}^{-1}
1	0.9464	0.0375	1.0483
2	1.0152	0.0505	1.2438
3	1.0213	0.0534	1.2985
4	1.0214	0.0535	1.3021
5	1.0214	0.0535	1.3021

Table 2. Convergence pattern of the inverse overlap matrix S^{-1} for solid LiH (NaCl structure, lattice constant $a = 3.803$ [b]). The basis set used is α) of Table 7

2^n terms of the series; by suitable choice of λ the convergence behaviour can be controlled, for $\lambda = 0.5$ rapid convergence has been achieved in all cases treated so far. Table 2 shows the convergence pattern for solid LiH (minimal basis set).

Using the exact S^{-1} we can write the many-body expansion for ρ in a form similar to that given by Magnasco and Musso [18]

$$\rho = \sum_i \rho_i + \sum_i \Delta\rho_i + \sum_{ij} \Delta\rho_{ij} \tag{9}$$

with

$$\begin{aligned} \rho_i + \Delta\rho_i &= \sum_\alpha |\alpha i\rangle \langle \alpha i| \\ \Delta\rho_{ij} &= \sum_{\alpha\beta} |\alpha i\rangle (S^{-1}_{\alpha i, \beta j} + \delta_{\alpha i, \beta j} \\ &\quad - \tfrac{1}{2} \sum_{\substack{k=i,j \\ \gamma}} [S_{\alpha i, \gamma k} S^{-1}_{\gamma k, \beta j} + S^{-1}_{\alpha i, \gamma k} S_{\gamma k, \beta j}]) \langle \beta j| \end{aligned}$$

Here ρ_i is the least-squares fitted electron density of subsystem i; $|\alpha i\rangle$ denotes orbital α of subsystem i. The corrections $\Delta\rho_i$, $\Delta\rho_{ij}$ correspond to a vanishing charge

$$\mathrm{Tr}(\Delta\rho_i) = \mathrm{Tr}(\Delta\rho_{ij}) = 0 \tag{10}$$

With (9) convergence of the many-body expansion is guaranteed. For the total energy at most four-body corrections occur. The two-body approximation includes basically the following terms

$$\begin{aligned} &h\, \Delta\rho_{ij}, \quad \sum_k \rho_k\, \Delta\rho_{ij}, \quad \rho_i\, \Delta\rho_j, \\ &\Delta\rho_i\, \Delta\rho_j, \quad \Delta\rho_{ij}\, \Delta\rho_i, \quad \Delta\rho_{ij}\, \Delta\rho_{ij} \end{aligned} \tag{11a}$$

(Here h is the one-electron part of the Fock operator.) The three-body approximation contains additional terms

$$\Delta\rho_{ij}\, \Delta\rho_k, \quad \Delta\rho_{ij}\, \Delta\rho_{jk} \tag{11b}$$

the four-body approximation the terms

$$\Delta\rho_{ij}\, \Delta\rho_{kl} \tag{11c}$$

The first two terms in (11a) already represent the most important three-body contributions, which are essential in particular for metallic bonding [19, 20];

Table 3. Computation times for the LiH layer, solid LiH (lattice constant 3.8 [b]) and diamond (equilibrium geometry) using various basis sets for a) determination of localized orbitals, b) a two-body correction, c) a three-body correction

	Basis set	a)	b)	c)
solid LiH	$1s/1s$	2.98 sec	0.45 sec	0.78 sec
	$5s/5s$	38.0	13.0	33.0
LiH layer	$1s/1s$	1.04	0.33	0.58
	$5s/5s$	19.0	10.0	25.0
diamond	$2s/1p$	9.8	5.5	10.0

(11b) and (11c) do not contain any monopole–monopole interactions, and consequently should be comparatively small.

In order to judge relative computation times and orders of magnitude of the many-body contributions to the total energy, we give in Tables 3 and 4 examples for LiH layers, solid LiH and diamond. From these we can see that the calculation of the many-body terms requires virtually the same amount of time as the calculation of the localized orbitals and that the convergence is satisfactory even in the case of diamond, where the orbital overlap is very strong.

3. Application to LiH

3.1. The LiH molecule

Results for total energy, equilibrium distance and force constant are given in Table 5. Each subsystem in our calculations consisted of one orbital; to describe the polarization of the orbital localized on H one basis function in the bond midpoint (*b* in Table 7) and an additional function on Li (*c* in Table 7) were used. The results are in each case compared with conventional HF results. The agreement is satisfactory.

3.2. The LiH layer

Three different basis sets were used. Table 6 shows the order of magnitude of various two- and three-body corrections, equilibrium lattice constants, total energy,

Table 4. Total energies in a) the one-body, b) the two-body, c) the three-body approximation for the LiH layer, solid LiH (lattice constant 3.8 [b]) and diamond (equilibrium geometry) using various basis sets

	Basis set	a)	b)	c)
solid LiH	$1s/1s$	−6.7218 [h]	−6.6730 [h]	−6.6718
	$5s/5s$	−8.1499	−8.0340	−8.0320
LiH layer	$1s/1s$	−6.7129	−6.6607	−6.6600
	$5s/5s$	−8.1274	−8.0301	−8.0295
diamond	$2s/1p$	−77.4007	−72.3574	−72.3926

Table 5. Total energy E, equilibrium distance a and force constant K for the LiH molecule a) without, b) with basis function in the bond midpoint, c) with an additional basis function $\eta = 0.461$ at Li contributing to the orbital localized on H. In every second column results from conventional HF calculations are given

Basis set: Li s: 111.0, 28.2, 7.19, 1.82, 0.461
H s: 13.71, 3.425, 0.856, 0.214, 0.054
bond-midpoint: 0.21

	E [h]		a [b]		K [mdyn/Å]	
a)	−7.9502	−7.9520				
b)	−7.9616	−7.9723	3.158	3.051	1.312	1.221
c)	−7.9703	−7.9723	3.058	3.051	1.227	1.221

lattice energy and the second derivative of the total energy with respect to the lattice constant, each in the two- and the three-body approximation. The results show that it is important to exceed the minimum basis quality.

Table 6. Order of magnitude for various two-body and three-body corrections, equilibrium lattice constant a, total energy E, lattice energy E_g, $K = \partial^2 E/\partial a^2$ for the LiH layer (cubic lattice structure) using basis sets α), β), γ). In the last four rows the upper entries refer to two-body, the lower entries to three-body results

Basis sets:
α) Li: 1.995
H: 0.187
β) Li: 111.0, 28.2, 7.19, 1.82, 0.461
H: 13.71, 3.425, 0.856, 0.214, 0.054
γ) Li: 921.271, 138.73, 31.9415, 9.35329, 3.15789, 1.15685, 0.44462
H: 148.273, 22.174, 4.9701, 1.3704, 0.43666, 0.15585, 0.06074

	α)	β)	γ)
2-body corrections [h]			
Li–H	$8\cdot10^{-3}$	$2\cdot10^{-2}$	$2\cdot10^{-2}$
H–H	$6\cdot10^{-3}$, -10^{-4}	$2\cdot10^{-2}$, 10^{-4}	10^{-2}, $-3\cdot10^{-4}$
3-body corrections [h]			
H–Li–H	$1\cdot10^{-4}$	$3\cdot10^{-4}$	$3\cdot10^{-4}$
H–H–H	$-1\cdot10^{-6}$	$-9\cdot10^{-5}$	$5\cdot10^{-6}$
a [b]	3.669	3.746	3.770
	3.688	3.756	3.792
E [h]	−6.6609	−8.0301	−8.0459
	−6.6601	−8.0295	−8.0447
E_g [h]	0.3613	0.3191	0.3265
	0.3605	0.3185	0.3253
K [mdyn/Å]	2.42	1.13	1.21
	2.50	1.17	1.22

3.3. *Solid LiH*

Table 7 gives the equilibrium properties for solid LiH in the NaCl structure, Table 8 for LiH in the CsCl structure. The partioning of the two- and three-body corrections according to different energy contributions shows that the Coulomb terms are by no means negligible compared with the exchange terms, in contrast to the assertion of Gordon and Kim [21]. Experimental results are 3.87 [b] for the equilibrium lattice constant and 0.346 [h] for the lattice energy of LiH in the NaCl structure. The results with basis set α) are in satisfactory agreement with the FSGO calculations of Erickson and Linnett [22] (−6.673 [h] for the total energy and 3.803 [b] for the lattice constant).

4. Conclusion

Using direct localization and approximating the interaction between orbital groups belonging to different localization centres, the effort for calculating localized HF orbitals can be reduced to the magnitude of the effort necessary in the case of isolated subsystems. The evaluation of quantities such as the total energy, orbital

Table 7. Order of magnitude for various two-body and three-body corrections, partitioning of the total two-body and three-body correction according to different energy contributions, equilibrium lattice constant a, total energy E, lattice energy E_g, and $K = \partial^2 E/\partial a^2$ for solid LiH (NaCl structure)

Basis sets: α) Li: 1.995 H: 0.204 β), γ) as in Table 6	α)	β)	γ)
2-body corrections [h]			
Li–H	$6\cdot 10^{-3};\ 1\cdot 10^{-6}$	$1\cdot 10^{-2};\ -9\cdot 10^{-5}$	$1\cdot 10^{-2};\ -4\cdot 10^{-5}$
H–H	$3\cdot 10^{-3};\ -9\cdot 10^{-5}$	$9\cdot 10^{-3};\ -1\cdot 10^{-4}$	$5\cdot 10^{-3};\ -3\cdot 10^{-4}$
3-body corrections [h]			
H–Li–H	$6\cdot 10^{-5}$	$1\cdot 10^{-4}$	$2\cdot 10^{-4}$
H–H–H	$9\cdot 10^{-5}$	$9\cdot 10^{-5}$	$2\cdot 10^{-4}$
2- and 3-body contributions of			
kinetic energy	$4\cdot 10^{-2};\ 0$	$1\cdot 10^{-1};$	
electron-nucleus energy	$3\cdot 10^{-3};\ 5\cdot 10^{-6}$	$-8\cdot 10^{-2};$	
electron-electron energy (Coulomb part)	$3\cdot 10^{-2};\ 2\cdot 10^{-4}$	$1\cdot 10^{-1};$	
exchange energy	$-2\cdot 10^{-2};\ 1\cdot 10^{-3}$	$-6\cdot 10^{-2};$	
a [b]	3.772	3.986	3.938
	3.806	4.009	3.999
E [h]	−6.6734	−8.0345	−8.0548
	−6.6719	−8.0328	−8.0520
E_g [h]	0.3738	0.3235	0.3354
	0.3723	0.3218	0.3326
K [mdyn/Å]	2.32	0.65	1.02
	2.39	0.78	1.08

Table 8. Order of magnitude for various two-body and three-body corrections, equilibrium lattice constant a, total energy E, lattice energy E_g, and $K = \partial^2 E/\partial a^2$ for solid LiH (CsCl structure) using basis sets α), γ). In the last four rows the upper entries refer to two-body, the lower entries to three-body results

Basis sets:
α) Li: 1.993 H: 0.23
γ) as in Table 6, but without $\eta = 0.0607$

	α)	γ)
2-body corrections [h]		
Li–H	$5 \cdot 10^{-3}$	$6 \cdot 10^{-3}$
H–H	$3 \cdot 10^{-2}$; $-2 \cdot 10^{-3}$; $3 \cdot 10^{-5}$	$2 \cdot 10^{-2}$; $-2 \cdot 10^{-3}$; $-8 \cdot 10^{-7}$
3-body corrections [h]		
H–Li–H	$2 \cdot 10^{-4}$	$3 \cdot 10^{-4}$
H–H–H	$-5 \cdot 10^{-5}$	$-2 \cdot 10^{-5}$
a [b]	4.720	4.790
	4.713	4.820
E [h]	−6.6473	−8.0327
	−6.6469	−8.0311
E_g [h]	0.3477	0.3133
	0.3473	0.3117
K [mdyn/Å]	3.58	1.69
	3.57	1.60

energies etc. from the non-orthogonal localized orbitals can be performed with the help of many-body corrections. Two-body corrections often prove to be sufficient. In this case, the total computational effort is comparable with that of a conventional HF calculation for pairs of orbital groups.

References

1. Foster, J. M., Boys, S. F.: Rev. Mod. Phys. **32**, 300 (1960)
2. Edmiston, C., Ruedenberg, K.: Rev. Mod. Phys. **35**, 457 (1963)
3. Trindle, C., Sinanoglu, O.: J. Chem. Phys. **49**, 65 (1968)
4. England, W., Gordon, M. S.: J. Am. Chem. Soc. **91**, 6864 (1969)
5. Niessen, W. v.: J. Chem. Phys. **56**, 4290 (1970); Theoret. Chim. Acta (Berl.) **33**, 7 (1974)
6. Barr, R., Basch, H.: Chem. Phys. Letters **32**, 537 (1975)
7. Adams, W. H.: J. Chem. Phys. **34**, 89 (1961); Phys. Rev. Letters **32**, 1093 (1974)
8. Gilbert T. L., in: Molecular orbitals in chemistry, physics and biology, P. Löwdin, B. Pullman, eds. New York: Academic Press 1964
9. Peters, D.: J. Chem. Phys. **46**, 4427 (1968)
10. Wilhite, D. L., Whitten, J. L.: J. Chem. Phys. **58**, 948 (1973)
11. Anderson, P. W.: Phys. Rev. **181**, 25 (1969)
12. Daudey, J. P.: Chem. Phys. Letters **24**, 574 (1974)
13. Kambara, T.: J. Phys. Soc. Jap. **39**, 187 (1975); Prog. Theoret. Phys. **55**, 1335 (1976)
14. Gilbert, T. L., Kunz, A. B.: Phys. Rev. **B10**, 3706 (1974)
15. Kunz, A. B.: Phys. Stat. Sol. **36**, 301 (1969); **46**, 385 (1971)

16. Kunz, A. B.: J. Phys. **B6**, L47 (1973)
17. Otto, P., Ladik, J.: Chem. Phys. **8**, 192 (1975); **19**, 209 (1977)
18. Magnasco, V., Musso, G. F., Figari, G.: J. Chem. Phys. **60**, 3744 (1974); **64**, 220 (1976)
19. Harrison, W. A., in: Interatomic potentials and simulation of lattice defects, Gehlen, P. C., Beeler, J. L., Jaffee, R. I., eds. New York: Plenum Press 1972
20. Kolos, W., Nieves, F., Novaro, O.: Chem. Phys. Letters **41**, 431 (1976)
21. Gordon, R. G., Kim, Y. S.: J. Chem. Phys. **56**, 3122 (1972); **61**, 1 (1974)
22. Erickson, W. D., Linnett, J. W.: Faraday Trans. II **68**, 693 (1972)

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