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On the Use of Local Basis Sets for Localized Molecular Orbitals

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Two procedures are discussed for the direct variational optimization of localized molecular orbitals which are expanded in local subsets of the molecular basis set. It is shown that a Newton–Raphson approach is more efficient than an iterative diagonalization scheme. The effect of the basis-set truncation on the quality of *ab-initio* SCF results is investigated for Be, Li_2, HF, H_2O, NH_3, CH_4 and C_2H_6.

Key words: Localized molecular orbitals – Local basis sets – Direct energy minimization.

1. Introduction

The main reasons for the use of localized molecular orbitals (LMO's) in quantum chemical studies are their connection with classical chemical concepts, their usefulness in isolating functional groups within chemically related molecules, and the possibility of transferring LMO's from one molecule to other ones with similar structure.

In most cases LMO's are constructed from canonical SCF orbitals by way of a unitary transformation (a recent review is given in [1]; cf. also [2], [3]). The resulting LMO's are more or less localized on an atom or in a bond, but have so-called orthogonalization tails extending over the whole molecule. These orthogonalization tails have to be truncated, for practical reasons, when using the LMO's for the purposes mentioned above. The corresponding energy error is usually not very large, but by no means negligible (~ 1.5 eV) [4].

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A variational deorthogonalization of the LMO's before truncation does not seem to improve the situation: Sundberg et al. [5] obtained LMO's, which were still fairly orthogonal to each other and did not exhibit a spectacular increase in localization; in particular, the tails did not vanish.

An alternative is the direct determination of LMO's. If for each localization centre (atom or bond) a separate local basis set is used (i.e. a subset of the total molecular basis set, consisting of functions centred on or near a given atom or bond), tails can be explicitly excluded.

Such local basis sets have been discussed by several authors. Matsuoka [6] and the present authors [7] have modified the Adams–Gilbert equations [8] for this case. Mehler [9] has derived a variational method for non-orthogonal group functions based on local energy functionals. In these methods, however, there is no guarantee that those LMO's are obtained which – for the given local basis sets – lead to the lowest energy, when inserted in the Hartree-Fock (HF) energy expression. This has been claimed by Payne [10], but it has been shown by the present authors [11] that the derivation of Payne's equations was erroneous.

In this paper, we want to show that Payne's equations can be easily modified in such a way as to lead to the desired result. Furthermore, a second method – a modified Newton–Raphson procedure – is presented which also yields the variationally "best" LMO's. In Sect. 2 the two methods are described and their convergence properties are discussed. Applications to Be, Li_2, FH, H_2O, NH_3, CH_4, C_2H_6 are given in Sect. 3.

2. Methods

We start from a set of basis functions, which is partitioned into subsets $\{|\chi_{ip}\rangle\}$, where i is the number of the subset and p the number of a basis function within a given subset. We assume that each subset corresponds to a certain localization centre (atom, lone pair, bond), i.e. includes only basis functions localized on or near this centre. We now require that a correspondence may be established between the localization centres and the (occupied) LMO's so that we can label the LMO's $\{|\varphi_{i\alpha}\rangle\}$ in a similar way as the basis functions, where i now denotes the localization centre and α distinguishes between different orbitals which can be attributed to the same centre. This one-to-one correspondence leads, in a natural way, to the following approximation for the (occupied) LMO's

$$|\varphi_{i\alpha}\rangle = \sum_p C_{ip,i\alpha} |\chi_{ip}\rangle \tag{1}$$

where all $C_{ip,j\alpha}$ with $i \neq j$ are constrained to be zero. This means that each LMO is expanded in basis functions of the corresponding subset, *a priori* excluding tails which might be described by basis functions of other subsystems.

Two remarks are in order here:

In the first place, the constraint (1) does not, in itself, provide LMO's which are "best localized" according to some localization criterion (as e.g. the Foster–Boys

[12] or Edmiston–Ruedenberg [13] LMO's), nor do they exhibit minimum (absolute) overlap with LMO's from adjacent localization centres. The block-structure of the orbital-coefficient matrix $C_{ip,j\alpha}$ is advantageous, however, when transferring LMO's from one molecule to another. (In addition, this block-structure leads, in a natural way, to approximations for the interactions of electrons in different LMO's, which reduce the computational effort for *ab-initio* calculations in a drastic way [7], [14].)

Secondly, the LMO's in Eq. (1) have to be non-orthogonal, when belonging to different localization centres $i \neq j$. This has nothing to do with the degree of localization, as discussed e.g. in [15], but is simply due to the fact that the number of non-zero coefficients in $C_{ip,j\alpha}$ would not be enough, generally, to meet the orthogonality requirements. Consider the simple case that there are m orbitals, each expanded in n basis functions; then the number of non-zero coefficients is nm, while the number of orthonormality relations is $m(m+1)/2$; these relations cannot in general be satisfied, consequently, for $m > 2n-1$.

We now search for the Slater determinant with the lowest energy, which can be built up from the non-orthogonal orbitals $|\varphi_{i\alpha}\rangle$ in Eq. (1). With the usual definition for the one-electron part h of the Hamiltonian H and the Fock operator F, the total electronic energy E for a closed-shell molecule reads

$$E = \sum_{i\alpha}^{\text{occ}} \langle \varphi_{i\alpha} | h + F | \tilde{\varphi}_{i\alpha} \rangle \tag{2}$$

where the reciprocal orbitals $|\tilde{\varphi}_{i\alpha}\rangle$ are defined as follows

$$|\tilde{\varphi}_{i\alpha}\rangle = \sum_{j\beta}^{\text{occ}} |\varphi_{j\beta}\rangle S^{-1}_{j\beta,i\alpha} \tag{3}$$

($S^{-1}_{j\beta,i\alpha}$ is the inverse overlap matrix of the orbitals (1)). Varying E with respect to the (occupied) LMO $|\varphi_{j\beta}\rangle$, we get

$$\delta_{(j\beta)}E = 2\left(\langle \delta\varphi_{j\beta} | F | \tilde{\varphi}_{j\beta} \rangle + \sum_{i\alpha} \langle \varphi_{i\alpha} | F | \delta_{(j\beta)} \tilde{\varphi}_{i\alpha} \rangle \right). \tag{4}$$

Using the relation

$$\delta S^{-1} = -S^{-1} \cdot \delta S \cdot S^{-1}, \tag{5}$$

the dependence of the $|\delta\tilde{\varphi}_{i\alpha}\rangle$ on $|\delta\varphi_{j\beta}\rangle$ is easily established:

$$|\delta_{(j\beta)}\tilde{\varphi}_{i\alpha}\rangle = (1-\rho)|\delta\varphi_{j\beta}\rangle \cdot S^{-1}_{j\beta,i\alpha} - |\tilde{\varphi}_{j\beta}\rangle\langle \delta\varphi_{j\beta} | \tilde{\varphi}_{i\alpha}\rangle, \tag{6}$$

with the density matrix

$$\rho = \sum_{k\gamma}^{\text{occ}} |\tilde{\varphi}_{k\gamma}\rangle\langle\varphi_{k\gamma}| = \sum_{k\gamma}^{\text{occ}} |\varphi_{k\gamma}\rangle\langle\tilde{\varphi}_{k\gamma}|. \tag{7}$$

Inserting Eq. (6) into Eq. (4) yields

$$\delta_{(j\beta)}E = 4\langle \delta\varphi_{j\beta} | (1-\rho) F | \tilde{\varphi}_{j\beta} \rangle \tag{8}$$

and, finally,

$$\frac{\partial E}{\partial C_{jq,j\beta}} = 4\langle \chi_{jq}|(1-\rho)F|\tilde{\varphi}_{j\beta}\rangle. \tag{9}$$

The lowest energy is achieved, if the energy gradient (9) vanishes for all j, q, β:

$$\langle \chi_{jq}|(1-\rho)F|\tilde{\varphi}_{j\beta}\rangle = 0. \tag{10}$$

We now describe two methods for the determination of the orbital coefficients $C_{ip,i\alpha}$ in Eq. (1), so that the $C_{ip,i\alpha}$ satisfy the conditions (10).

In a first approach, we cast Eq. (10) into eigenvalue form. We define a partial density matrix for the subsystem j

$$\rho^{(j)} \equiv \sum_{\gamma} |\tilde{\varphi}_{j\gamma}\rangle\langle\varphi_{j\gamma}| \tag{11}$$

with the properties

$$\rho^{(j)}|\tilde{\varphi}_{i\beta}\rangle = \delta_{ij}|\tilde{\varphi}_{i\beta}\rangle \tag{12}$$

and, if orbitals belonging to the same localization centre are chosen to be mutually orthogonal (cf. Eq. (18) below),

$$\rho^{(j)}|\varphi_{j\beta}\rangle = |\tilde{\varphi}_{j\beta}\rangle. \tag{13}$$

Using Eq. (11), the left-hand side of Eq. (10) can be transformed to

$$\langle \chi_{jq}|(1-\rho)F(1-\rho+\rho^{(j)})|\varphi_{j\beta}\rangle; \tag{14}$$

this means that Eq. (10) is equivalent to

$$\langle \chi_{jq}|\tilde{F}^{(j)} - \varepsilon_{j\beta}|\varphi_{j\beta}\rangle = 0 \tag{15}$$

with

$$\tilde{F}^{(j)} = (1-\rho+\rho^{(j)T})F(1-\rho+\rho^{(j)}) \tag{16}$$

and

$$\varepsilon_{j\beta} = \langle\tilde{\varphi}_{j\beta}|F|\tilde{\varphi}_{j\beta}\rangle. \tag{17}$$

The eigenvalue problem in Eq. (15) has to be solved separately for each subsystem, but for each j only the space spanned by the corresponding local basis set is involved. The resulting orbitals fulfil the (partial) orthonormality relations

$$\langle\varphi_{j\beta}|\varphi_{j\gamma}\rangle = \delta_{\beta\gamma}. \tag{18}$$

An equation similar to Eq. (15) has been given recently by Payne [16], but his subsequent replacement

$$\rho^{(j)} \rightarrow \hat{\rho}^{(j)} = \sum_{\gamma} |\varphi_{j\gamma}\rangle\langle\varphi_{j\gamma}|$$

[10] is only correct in two cases: (a) if orbitals from different subsystems are mutually orthogonal, or (b) if a common basis set is used for all subsystems; those cases have been explicitly excluded in our discussion here.

Our experience with the solution of Eq. (15) indicates that, in the HF iterations with the modified Fock operator $\tilde{F}$, the convergence may be extremely slow – in particular near the energy minimum – so as to render the method nearly impractical. The reasons are the following:

(a) the $\tilde{F}^{(i)}$ contain orbital coefficients $C_{ip,i\alpha}$ up to the sixth order (while only the second order is involved in the standard HF procedure); this may lead to similar convergence problems as in MC-SCF (cf. e.g. [17]).

(b) the diagonalization of $\tilde{F}^{(j)}$ in the basis $\{|\chi_{jq}\rangle\}$ is equivalent to that of F in the basis

$$|\chi'_{jq}\rangle = (1-\rho+\rho^{(j)})|\chi_{jq}\rangle \tag{19}$$

as suggested by Peters [18]; because of

$$\langle\chi'_{jq}|\varphi_{i\alpha}\rangle = 0 \qquad (i \neq j) \tag{20}$$

no simultaneous admixing of both virtual orbitals and occupied LMO's from other localization centres to a given

$$|\varphi'_{j\beta}\rangle = (1-\rho+\rho^{(j)})|\varphi_{j\beta}\rangle \tag{21}$$

can take place in a single iteration step; this may affect the convergence of the LMO's in an unfavourable way.

We now turn to a second method of determining the orbital coefficients $C_{ip,i\alpha}$ subject to the conditions (10), a direct minimization method.

Direct minimization of the SCF energy for orthogonal orbitals has been dealt with in a number of papers ([19] to [22]); we introduce it here for LMO's expanded in local basis sets, in a similar way as discussed by us previously in a different context [14].

In order to satisfy Eq. (10), we have to search for a local minimum of the energy function $E(\{C_{jq,j\beta}\})$. If some guess $\{C^{(0)}_{jq,j\beta}\}$ for the orbital coefficients in Eq. (1) is known, $E(\{C_{jq,j\beta}\})$ can be approximated by a Taylor series in $\Delta C_{jq,j\beta} \equiv C_{jq,j\beta} - C^{(0)}_{jq,j\beta}$ up to second order, for $\Delta C_{jq,j\beta}$ not too large. In the Taylor series, we need the energy gradient $\partial E/\partial C_{iq.j\beta}|_{C^{(0)}}$ which is given by Eq. (9), and the Hessian matrix $\partial^2 E/\partial C_{jq,j\beta}\,\partial C_{kr,k\gamma}|_{C^{(0)}}$ which can be evaluated in the following way:

We vary $\delta_{(j\beta)}E$ from Eq. (8) with respect to $|\varphi_{k\gamma}\rangle$ and get, neglecting the dependence of F on $|\varphi_{k\gamma}\rangle$,

$$\delta_{(k\gamma)}(\delta_{(j\beta)}E) \approx 4(-\langle\delta\varphi_{j\beta}|\delta_{(k\gamma)}\rho \cdot F|\tilde{\varphi}_{j\beta}\rangle + \langle\delta\varphi_{j\beta}|(1-\rho)F|\delta_{(k\gamma)}\tilde{\varphi}_{j\beta}\rangle). \tag{22}$$

Inserting in Eq. (22) the relations

$$\delta_{(k\gamma)}\rho = |\delta\varphi_{k\gamma}\rangle\langle\tilde{\varphi}_{k\gamma}| + \sum_{i\alpha} |\varphi_{i\alpha}\rangle\langle\delta_{(k\gamma)}\tilde{\varphi}_{i\alpha}| \tag{23}$$

and (cf. Eq. (6))

$$|\delta_{(k\gamma)}\tilde{\varphi}_{j\beta}\rangle = (1-\rho)|\delta\varphi_{k\gamma}\rangle \cdot S^{-1}_{k\gamma,j\beta} - |\tilde{\varphi}_{k\gamma}\rangle \cdot \langle\delta\varphi_{k\gamma}|\tilde{\varphi}_{j\beta}\rangle \tag{24}$$

we obtain

$$\frac{\partial^2 E}{\partial C_{jq,j\beta}\,\partial C_{kr,k\gamma}} \approx 4\Big(A(F)_{jq,kr}\,S^{-1}_{k\gamma,j\beta} - A(1)_{jq,kr}\langle\tilde{\varphi}_{k\gamma}|F|\tilde{\varphi}_{j\beta}\rangle \\ -\langle\chi_{jq}|\tilde{\varphi}_{k\gamma}\rangle B_{kr,j\beta} - \langle\chi_{kr}|\tilde{\varphi}_{j\beta}\rangle B_{jq,k\gamma}\Big) \tag{25}$$

with

$$A(X)_{jq,kr} = \langle\chi_{jq}|(1-\rho)X(1-\rho)|\chi_{kr}\rangle \tag{26}$$

and

$$B_{jq,k\gamma} = \langle\chi_{jq}|(1-\rho)F|\tilde{\varphi}_{k\gamma}\rangle. \tag{27}$$

When minimizing E, one may require that orthonormality is preserved within each subsystem j. This is possible, without loss of generality, since E is constant with respect to arbitrary linear transformations between the orbitals $\varphi_{i\alpha}$. The constraint is necessary in order to avoid large changes $\Delta C_{jq,j\beta}$ of the orbital coefficients, which would make the Taylor expansion up to second order for $E(\{C_{jq,j\beta}\})$ unreliable. To first order, the constraints read

$$\sum_{q,r} S_{jq,jr}(\Delta C_{jq,j\beta}\,C^{(0)}_{jr,j\gamma} + \Delta C_{jr,j\gamma}\,C^{(0)}_{jq,j\beta}) = 0 \tag{28}$$

The minimization of the Taylor series approximation to E (with Eqs. (9) and (25)) under the constraints (28) leads to a set of linear equations for $\{\Delta C_{jq,j\beta}\}$ which can be solved by standard methods, to yield an improved guess $\{C^{(1)}_{jq,j\beta}\}$ for the orbital coefficients in Eq. (1). The procedure has then to be repeated until self-consistency is reached.

Some remarks are in order here:

Firstly, if there is a one-to-one correspondence between i and α (i.e. if each LMO has its own local basis set), the Hessian matrix (25) has dimension N, where N is the total number of basis functions; furthermore, in this case the constraints (28) reduce to m normalization conditions, where m is the total number of orbitals involved. The procedure described above is then comparable to a standard HF calculation with respect to storage requirements and computation time. (Note that two-electron integrals enter Eq. (25) only via the Fock matrix F.)

Secondly, the constraints (28) alone are not sufficient, in general, to guarantee the non-singularity of the Hessian matrix [20]. This problem is not as pressing, however, as in the standard SCF case, because only unitary transformations within the individual subsystems have to be considered here. If each LMO is expanded in a separate local basis set, singularities are excluded anyway.

Thirdly, the final result of the iterative procedure does not depend on the approximations in Eqs. (22) and (28). Only the rate of convergence is affected. In our applications, the convergence was typically as fast as, or even faster than that in standard SCF calculations with comparable basis sets. For cases with an inappropriate starting guess $\{C^{(0)}_{jq,j\beta}\}$ it may be advantageous, however, to replace

Table 1. Total energy E (in a.u.) for Be. Basis set: 7*s* [23], partitioned into subsets in different ways (see text)

Local basis sets Core	 Valence	E
4*s*	4*s*	−14.55278
5*s*	4*s*	−14.56621
5*s*	5*s*	−14.56622
6*s*	5*s*	−14.56722
Standard SCF		−14.56723

Eq. (25) by a matrix with the same eigenvectors and the same positive eigenvalues, but with the negative eigenvalues replaced by zero.

3. Applications

The influence of basis set partitioning between the 1*s* and 2*s* orbitals is shown for Be in Table 1.

The local basis set for 1*s* includes the k functions with highest exponents out of the 7*s* Gaussian basis set of Roos and Siegbahn [23], while for the 2*s* local basis the k' functions with lowest exponents are chosen. If the two local basis sets have only one function (with medium exponent) in common ($k = k' = 4$), the deviation from the standard SCF result is only 0.4 eV; this deviation is largely due to deficiencies of the core: if k is enlarged to 5, the error is reduced to 0.03 eV. This result is in line with the findings of Dunning and Hay [24], that, in a segmented contraction scheme, it is sufficient, to attribute one primitive function with medium exponent to both the 1*s* and the 2*s* group.

Results for Li_2 are given in Table 2. Each of the two local basis sets for the $(1s^2)$-cores includes the k *s*-functions with highest exponents out of the 4*s*/1*p* atomic basis set, while the valence orbital is expanded in the k' *s*-functions with lowest exponents (and the *p*-functions) from both atoms. With no "overlapping" functions (i.e. $k = k' = 2$), the errors in the total energy and bond length are

Table 2. Total energy E (in a.u.), bond length r_e (in a.u.), and force constant k (in a.u.; calculated at the experimental bond length 5.05 a.u.) for Li_2. Basis set: 4*s*/1*p* (contracted from 5*s*/1*p*; exponents: (16.1, 2.94), 0.795, 0.075, 0.03, 0.12), partitioned into subsets in different ways

Local basis sets Core	 Valence	E	r_e	k
2*s*	2*s*/1*p*	−14.6667	5.42	0.020
3*s*	2*s*/1*p*	−14.6690		
2*s*	3*s*/1*p*	−14.6756	5.31	0.018
3*s*	3*s*/1*p*	−14.6780		
Standard SCF		−14.6786	5.32	0.019

Table 3. Calculated bond lengths r_e (in a.u.), bond angles φ_e ($\sphericalangle$HXH), and total energies E (in a.u.; taken at the equilibrium distances, with the exception of CH_4, where values at the calculated bond length are given) for the isoelectronic molecules CH_4, H_2O, NH_3, FH. Basis sets: STO-3G, with p-functions in the direction of the bonds. Values in brackets: standard SCF results

	Local basis sets		Non-bonding orbital(s) and lone-pair(s)	E	r_e	φ_e
Molecule	Core	Bond orbitals(s)				
FH	$1s$(F)	$2p_\sigma$(F), $1s$(H)	$2s$(F)/$2p_\pi$(F)	−98.5606	1.812	
				(−98.5708)	(1.807)	
H_2O	$1s$(O)	$2s$(O), $2p_\sigma$(O), $1s$(H)	$2p_\pi$(O)/$2s$(O),	−74.9598	1.870	100.4°
			$2p_\sigma$(O)	(−74.9629)	(1.871)	(100.0°)
NH_3	$1s$(N)	$2s$(N), $2p$(N), $1s$(H)	$2s$(N), $2p$(N)	−55.4493	1.947	104.2°
				(−55.4540)	(1.952)	(104.2°)
CH_4	$1s$(C)	$2s$(C), $2p$(C), $1s$(H)		−39.7213	2.048	
				(−39.7269)	(2.047)	

0.32 eV and 0.05 Å, respectively. By adding one basis function per atom to the valence set ($k' = 3$) one gets results which are virtually identical with those of a standard SCF calculation.

Table 3 shows bond lengths and total energies for the isoelectronic series CH_4, NH_3, H_2O, FH. STO-3G basis sets have been used, segmented into local subsets according to the following scheme. Different subsets are used for different LMO's. Core orbitals are described by $1s$ STO's, bond orbitals by $2s$ and $2p$ STO's (with the $2p$'s directed along the bond axes) together with a hydrogen $1s$ function (an exception is FH, where the $2s$ STO is only used for the non-bonding orbital); lone pairs are expanded in $2s$ and (suitably oriented) $2p$ STO's. Only the $2s$-function is common to more than one local basis set; a further redundancy occurs, however, for NH_3 and CH_4, where four $2p$-functions (one for each bond or lone-pair orbital) are implied. The restriction introduced by the use of the local basis sets leads to energies which are by 0.1 to 0.3 eV higher than energies from standard SCF calculations with STO-3G basis sets. The maximum error occurs for FH; we note that it can be reduced to 0.05 eV, if the bonding orbital and the non-bonding $2s$ orbital of FH are treated within the same subsystem.

For CH_4 we have also calculated LMO's with Payne's method [10] using the basis sets given above: the energy increases by 0.05 eV. A detailed comparison with the work of Matsuoka [6] is not possible, because his basis sets are different from ours; for CH_4 he obtains – with a similar definition of subsystems – energy deviations from standard SCF, which are larger than ours by 0.1 to 0.4 eV. The truncated LMO's for CH_4 (with a minimal STO basis) of Newton, Switkes and Lipscomb [4] yield an energy loss of 0.8 eV compared to standard SCF, which is 5 times greater than ours. Turning now from energies to equilibrium geometries, we may state that our LMO results are virtually of the same quality as the corresponding standard SCF ones: the maximum deviation in bond length is 0.005 a.u.

Calculated values for C_2H_6, our last example, are compiled in Table 4.

Table 4. Calculated bond lengths (in a.u.), bond angle, and total energy E (in a.u.) for staggered C_2H_6; total energy E (in a.u.) for eclipsed C_2H_6 and barrier of rotation ΔE (in kcal/mole). Values in brackets: standard SCF results. Energies are taken at the standard SCF geometry of staggered C_2H_6. Basis set: STO-3G, with p-functions in the direction of the bonds. Definition of the local basis sets: see text

	$E/\Delta E$	r_{CC}	r_{CH}	φ_e
Eclipsed	−78.2825 (−78.2978)			
Staggered	−78.2871 (−78.3038)	2.97 (2.91)	2.05 (2.05)	110.3° (108.2°)
Barrier of rotation	2.92(3.73)			

Again we employed a STO-3G basis set, with p-functions oriented along the bond axes. The partitioning of the basis set into local subsets was similar to that described above in connection with Table 3. The 1s STO is used for the core, to each σ-bond are attributed the 2s STO's and (suitably oriented) 2p STO's from adjacent C atoms and, in case, the 1s STO from an adjacent H atom.

The restriction, caused by the introduction of the local basis sets, leads to an increase in the total energy of ~0.5 eV (compared to ~2 eV for the truncated LMO's in [4]). While the CH bond length is virtually unaffected, the CC bond length changes by 0.06 a.u., which probably means that our local basis for the CC bond orbital is insufficient.

The good agreement of our rotation barrier with the experimental value (2.93 kcal/mole) is certainly fortuitous. Compared to a standard SCF calculation employing the same basis set it is smaller by 22%. This is somewhat better than the corresponding values 35% and 34%, obtained by Newton et al. [4] and by Payne [10]. It is far better than the rotation barrier, with bond orbitals constructed from symmetrically orthogonalized AO's, reported recently by Corcoran and Weinhold [25], which indicates the importance of a proper choice of the local basis sets.

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