Integral approximations for LCAO-SCF calculations

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Three-center approximations to the four-center integrals occurring in ab initio LCAO calculations are investigated. It is shown that significant gains in computer time can be obtained without sacrificing accuracy, if a suitable expansion basis is chosen.

1. Introduction

The evaluation and processing of four-index, two-electron integrals constitutes a significant bottleneck in many types of ab initio electronic structure calculations. Several approaches based on approximate re-expansions have been suggested to overcome this obstacle. The numerical experience has not been impressive so far. A thorough study was conducted by Van Alsenoy [1], who tried various basis sets and expansion coefficients in SCF calculations.

The essence of all these methods is that they attempt to (approximately) expand a product of basis functions in a new auxiliary basis set $\{\alpha_u\}$

$$\chi_p(r)\chi_q(r) \equiv |pq) \approx |\theta_{pq}) \equiv \sum_u C_u^{pq}\alpha_u = \alpha C^{pq} . \quad (1)$$

Similar ideas are often used in density functional technology. Even when a basis set is used for the expansion of the Kohn–Sham orbitals, the density is usually re-expanded in other basis sets [2]. One should note, however, that the demand on the expansion basis may be a lot higher in other types of LCAO calculations, where products that do not directly contribute to the density expansion must also be accurately represented. The similarity and differ-

ence between these expansions are illustrated in eq. (2) below,

$$\rho(r) = \sum_{pq} D_{pq}|pq) \approx \sum_u \left(\sum_{pq} D_{pq}C_u^{pq}\right)|u)$$

$$= \sum_u d_u|u) . \quad (2)$$

Clearly, for the representation of the density it is sufficient to determine coefficients C_u^{pq} corresponding to density matrix elements D_{pq} of significant magnitude. The expansion of every product $|pq)$ is clearly a more difficult task than the expansion of the total density. (Note, for instance, that the density of any closed-shell atom can be described as an expansion in only s-type functions.) In pseudospectral methods the density (or the potential from it) are also similarly expanded in an auxiliary basis, rather than in products [3]. The form of (1) may look similar to the Gaussian product theorem used in many methods for evaluating two-electron integrals over Gaussian basis functions [4]. In these expansions the expansion is exact, however, the expansion basis set is specific for each product (p, q), and the size of expansion basis for that expansion is therefore of the order N^2, N being the number of LCAO basis functions.

There are several ways to determine the expansion coefficients C_u^{pq} in (1). If we define a residual function

$$R_{pq}(r) = \chi_p \chi_q - \theta_{pq}, \tag{3}$$

we can apply several different criteria by which R_{pq} is to be minimized. The most obvious approach would be to minimize the norm $(R_{pq} R_{pq})$ with respect to C_u^{pq}. This leads to

$$C_u^{pq} = \sum_t (pqt) S_{tu}^{-1}, \tag{4a}$$

or

$$C^{pq} = \mathbf{S}^{-1} \mathbf{a}^{pq}, \tag{4b}$$

where $a_t^{pq} = (pqt)$ is a three-center overlap, and S_{uv} is an overlap in the auxiliary basis. Minimizing the self-repulsion of the residual, i.e. minimizing $(R_{pq}|R_{pq})$ would instead lead to

$$C_u^{pq} = \sum_t (pq|t) V_{tu}^{-1}, \tag{5a}$$

or

$$C^{pq} = \mathbf{V}^{-1} \mathbf{b}^{pq}, \tag{5b}$$

where $b_t^{pq} = (pq|t)$ and V_{uv} are three- and two-center electron repulsion integrals, respectively. More generally, we may define a residual repulsion $r_j = (B_j | R_{pq})$, where $\{B_j\}$ is an arbitrary set of functions. Minimizing $\sum_j r_j^2$ leads to $C^{pq} = (\mathbf{A}^\dagger \mathbf{A})^{-1} \mathbf{A}^\dagger \mathbf{d}^{pq}$ where $d_j^{pq} = (B_j | pq)$ and $A_{jk} = (B_j | \alpha_k)$. In the special case of $\{B_j\} = \{\alpha_u\}$ then $\mathbf{A} = \mathbf{A}^\dagger = \mathbf{V}$ and we obtain $C^{pq} = \mathbf{V}^{-1} \mathbf{b}^{pq}$ as before.

To summarize, this suggests at least three different ways to resolve a 4-center, 2-electron integral $(pq|rs)$ with three-center quantities,

$$(pq|rs) = \mathbf{a}^{pq\dagger} \mathbf{S}^{-1} \mathbf{V} \mathbf{S}^{-1} \mathbf{a}^{rs}$$
$$= \sum_{tuvw} (pqt) S_{tu}^{-1} V_{uv} S_{vw}^{-1} (rsw), \tag{6}$$

$$(pq|rs) = \mathbf{a}^{pq\dagger} \mathbf{S}^{-1} \mathbf{b}^{rs}$$
$$= \sum_{tuvw} (pqt) S_{tu}^{-1} (rs|u), \tag{7a}$$

$$(pq|rs) = \mathbf{b}^{pq\dagger} \mathbf{S}^{-1} \mathbf{a}^{rs}$$
$$= \sum_{tuvw} (pq|t) S_{tu}^{-1} (rsu), \tag{7b}$$

$$(pq|rs) = \mathbf{b}^{pq\dagger} \mathbf{V}^{-1} \mathbf{b}^{rs}$$
$$= \sum_{tuvw} (pq|t) V_{uv}^{-1} (rs|u). \tag{8}$$

In the following, these three approximations will be referred to as the SVS, S and V approximations, respectively. The S approximation is equivalent to projecting one of the orbital products (charge distributions) onto the space spanned by the auxiliary basis functions. The SVS approximation is the same approximation for both charge distributions in the two-electron integrals. Van Alsenoy's [1] approach was to use the S approximation with the additional requirements that the charge and the dipole moment are conserved. The purpose is to minimize the error in the Coulomb field associated with the charge distribution rather than the error in the overlap. This is however more directly done in the V approximation which aims to minimize the error in the integral itself. As a matter of fact, the V approximation is an inner projection similar to the Beebe–Linderberg [5] approximation which is based on the Cholesky decomposition of the two-electron integral matrix. In our case, we formulate the projection in terms of an auxiliary set of basis functions, rather than to generate the projection manifold explicitly from the original distributions.

We will also investigate how the accuracy is affected if the entire potential is approximated in a consistent way, in other words, if we write the Coulombic part of the Fock operator as

$$h_{\text{eff}} = -\sum_\mu \frac{Z_\mu}{|r - r_\mu|} + \int \frac{\rho(r')}{|r - r'|} \, dr'$$
$$= -\sum_\mu \frac{Z_\mu}{|r - r_\mu|} + \sum_{pq} D_{pq} \int \frac{\chi_p(r') \chi_q(r')}{r - r'} \, dr'. \tag{9}$$

Writing the basis function product $\chi_r \chi_s$ as

$$\chi_r \chi_s \approx \sum_v C_v^{rs} \alpha_v = \sum_{uv} a_u^{rs} S_{uv}^{-1} \alpha_v, \tag{10}$$

the Fock matrix contribution becomes

$$J_{rs} = \langle \chi_r h_{\text{eff}} \chi_s \rangle \approx \sum_{uv} a_u^{rs} S_{uv}^{-1}$$
$$\times \left(-\sum_\mu Z_\mu \zeta_v^\mu + \sum_{pq} D_{pq} b_v^{pq} \right), \tag{11}$$

where we have introduced the quantities

$$\zeta_v^\mu = Z_\mu \int \frac{\alpha_v}{|r - r_m|} \, dr \, . \tag{12}$$

Expression (11) corresponds to the S approximation introduced in (7). We could of course also use

$$\chi_r \chi_s = \sum_{uv} b_r^{rs} V_{uv}^{-1} \alpha_v \, , \tag{13}$$

which corresponds to the V approximation (8). It appears unjustified, and has been found ineffective, to use the SVS approximation (6) here, which would be equivalent to approximating $b^{pq} \approx \mathbf{V}\mathbf{S}^{-1} a^{pq}$ in the expression for the potential.

2. Expansion basis sets

The choice of an expansion basis is certainly a topic that requires extensive and lengthy experimentation. Van Alsenoy considered several options. However, in order to reproduce SCF total energies with good accuracy, it is necessary to reproduce the behavior of the exact expansion near the atomic nuclei. Therefore, the expansion basis set should in principle include all one-center products of the original basis set. This is most easily achieved if the expansion basis set is uncontracted, in which case it should have the sums of the orbital exponents (and L values) from the original basis.

Straightforward as it is, generating the auxiliary basis functions by summing up exponents of the original basis set turns out to be inefficient. Many exponents may fall within a small range which can lead to linear dependencies. This is solved as usual by diagonalizing the overlap matrix (or $\mathbf{V}$) and removing vectors corresponding to eigenvalues lower than some threshold. The main problem with this

method is that the size of the auxiliary basis set grows rapidly with the size of the system.

In the examples in section 3, we have used a different approach, where the auxiliary basis set is even-tempered and uncontracted. For example, the auxiliary s functions on a given atom are determined by doubling the largest and the smallest exponents of the original basis (giving the exponent range) and using a geometrical progression of exponents within that range. This simple procedure gives substantially smaller expansion sets than the previous, yet gives excellent results for the V approximation as will be shown below.

This is an area which can certainly be explored further, and we find it plausible that a clever choice of the auxiliary basis functions can reduce the computational costs further, and/or improve the accuracy.

3. Results

In all examples we have employed the ANO basis set by Widmark et al. [6], the 3s2p1d contraction of a 14s9p4d primitive set for carbon and the 2s1p contraction of a 8s4p primitive set for hydrogen. The auxiliary basis set (uncontracted) was generated as described in the previous section with a ratio of 3.0, giving a 14s13p13d8f auxiliary basis set for carbon and a 9s7p4d auxiliary set for hydrogen. Eigenvectors of the overlap matrix $\mathbf{S}$ (for the S and SVS approximations) or the $\mathbf{V}$ matrix (for the V approximation) for which the eigenvalues are lower than a threshold of 10^{-5} were removed. In table 1, we give for reference the geometries where all calculations were carried out. In the rows of tables 2 and 3 denoted by ANO, the auxiliary basis set used was the

Table 1
Geometries (au) used for all calculations

Molecule (symmetry)		x	y	z
$C_6H_6 (D_{6h})$	C	0.000000	2.639970	0.000000
	H	0.000000	4.688456	0.000000
$C_2H_2 (D_{2h})$	C	0.000000	0.000000	1.136671
	H	0.000000	0.000000	3.141671
$C_2H_6 (D_{3h}, D_{3d})$	C	0.000000	0.000000	1.457927
	H	0.000000	1.961307	2.157933

Table 2
Three-center approximations to the SCF [a] energies for the dissociation $C_6H_6 \rightarrow 3C_2H_2$; the acetylene energy E_a and error $\epsilon_a = E_a - E_a^{SCF}$ (au), the benzene analogues E_b and ϵ_b, respectively, and the dissociation energy D and error $\delta = D - D^{SCF}$ (kcal/mol)

Auxiliary basis	E_a	ϵ_a	E_b	ϵ_b	D	δ
SVS approximation						
ANO	−92.7430	−15.9055	−311.3906	−80.6326	20809	20654
sp/s	−76.9884	−0.1509	−233.2593	−2.5014	1439.6	1285.5
spd/sp	−76.8448	−0.0074	−233.3630	−2.6050	1774.9	1620.8
spdf/spd	−76.8455	−0.0081	−231.0061	−0.2481	294.57	140.45
S approximation						
ANO	−90.3759	−13.5385	−296.2732	−65.5153	15779	15624
sp/s	−76.3051	0.5324	−229.3793	1.3786	291.26	137.14
spd/sp	−76.8010	0.0364	−231.1201	−0.3622	449.89	295.77
spdf/spd	−76.8413	−0.0039	−230.8289	−0.0710	191.31	37.19
V approximation						
ANO	−77.3741	−0.5366	−232.8644	−2.1065	465.75	311.63
sp/s	−76.6842	0.1532	−230.3638	0.3942	195.24	41.13
spd/sp	−76.8345	0.0029	−230.7594	−0.0014	160.55	6.43
spdf/spd	−76.8373	0.0001	−230.7576	0.0003	154.16	0.04
V′ approximation						
ANO	−53.2830	23.5544	−168.2576	62.5004	5276.4	5122.2
sp/s	−76.6753	0.1622	−230.3653	0.3926	213.01	58.90
spd/sp	−76.8330	0.0045	−230.7565	0.0015	161.60	7.48
spdf/spd	−76.8369	0.0006	−230.7602	−0.0023	156.60	2.48

[a] $E_a^{SCF} = -76.8374$ au, $E_b^{SCF} = -230.7579$ au, $D^{SCF} = 154.12$ kcal/mol.

same as the original ANO basis set. This trivial choice is not expected to work well for SCF energies, but it has proven to be surprisingly useful for correlated energies [7]. In addition to the three approximations introduced in eqs. (6)–(8), tables 2 and 3 show results obtained with a fourth approximation, denoted by V′, corresponding to the V approximation with an analogous approximation in the nuclear attraction integrals (eqs. (9) and (13)).

In table 2, we present the energies of dissociation of benzene into three acetylene fragments. With an spd/sp expansion basis, the errors in the total V energies of benzene are typically only a few mE_h, and if f/d functions are included the error drops to a few tenths of a mE_h. The error with the SVS approximation is typically two orders of magnitude larger. The same trend is seen for the energy differences. The performance of the V approximation is impressive, especially for the largest expansion set. The general trend is that the SVS approximation is much worse,

and the S approximation somewhere between.

Finally, in table 3 we report calculations of the torsional barrier of ethane. The eclipsed conformation we used was obtained by a rigid rotation of one of the methyl groups in the staggered conformation. Here the S and SVS approximations even give the wrong sign, proving that they are completely unreliable for calculating geometries. The V approximation, again, gives an excellent result for the largest expansion basis.

To summarize, the V approximation gives accurate energies for the cases we have considered. The number of auxiliary basis functions that is required is of the order of $10N$, where N is the dimension of the original basis, as compared to N^2 in a full calculation. The gains in computing time will therefore be expected to be even more important for larger systems. We must also conclude that the results ar not improved by introducing the additional approximation in the one-electron integrals. As mentioned

Table 3
Three-center approximations to the SCF [a] torsional barrier in ethane; the eclipsed energy E_e and error $\epsilon_e = E_e - E_e^{SCF}$ (au), the staggered analogues E_s and ϵ_s respectively, and the barrier height ΔE and error $\delta = \Delta E - \Delta E^{SCF}$ (kcal/mol)

Auxiliary basis	E_e	ϵ_e	E_s	ϵ_s	ΔE	δ
SVS approximation						
ANO	−100.0084	−20.7612	−100.1453	−20.8924	85.907	82.335
sp/s	−79.7599	−0.5127	−79.9368	−0.6839	110.991	107.419
spd/sp	−79.4742	−0.2270	−79.5354	−0.2825	38.431	34.859
spdf/spd	−79.2565	−0.0093	−79.2486	0.0043	−4.969	−8.540
S approximation						
ANO	−93.1463	−13.8991	−93.2774	−14.0245	82.257	78.686
sp/s	−79.2883	−0.0411	−79.3183	−0.0654	18.847	15.285
spd/sp	−79.3371	−0.0899	−79.3595	−0.1066	14.008	10.436
spdf/spd	−79.2487	−0.0014	−79.2463	0.0066	−1.493	−5.065
V approximation						
ANO	−79.7207	−0.4735	−79.7208	−0.4679	0.045	−3.527
sp/s	−79.1013	−0.1459	−79.1081	0.1448	4.257	0.685
spd/sp	−79.2484	−0.0011	−79.2540	−0.0011	3.524	−0.048
spdf/spd	−79.2472	0.0000	−79.2529	0.0000	3.573	0.001
V' approximation						
ANO	−55.3656	23.8816	−55.3379	23.9150	−17.426	−20.998
sp/s	−79.0915	0.1557	−79.0966	0.1563	3.241	0.331
spd/sp	−79.2410	0.0062	−79.2461	0.0068	3.164	−0.408
spdf/spd	−79.2461	0.0011	−79.2517	0.0012	3.545	0.027

[a] $E_e^{SCF} = -79.2472$ au, $E_s^{SCF} = -79.2529$ au, $\Delta E^{SCF} = 3.572$ kcal/mol.

above, the V approximation can be seen as an inner projection of the two-electron operator. Similarly, the SVS approximation can be seen as an outer projection of the two-electron operator. The reason why this method performs much worse is found in the way in which the expansion coefficients are determined. In the S and the SVS approximations the expansion coefficients are determined to mimic the original charge distribution, whereas in the V approximation, the expansion coefficients are determined to mimic the Coulomb field of the original charge distribution, which is clearly more important for electron repulsion integrals.

We currently have no meaningful timings to report for these calculations, since they were all carried out with prototype versions of a new code, for which computational efficiency so far has not been an issue. However, we are confident that with proper code and algorithm optimization, this approach will be much faster than anything based on explicit evaluation of four-index quantities.

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