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Using the locality of the small-component density in molecular Dirac–Hartree-Fock calculations

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Abstract. A novel scheme to improve the computational efficiency of the Dirac–Hartree-Fock method was implemented and tested in different model systems. The method uses a one-center approximation to remove all multicenter electron-repulsion integrals over the small-component basis. In all cases we found the associated errors to be below chemical accuracy, which makes the method suitable for routine application to molecules that contain heavy elements.

Key words: Relativistic quantum chemistry – Four component calculations – Linear scaling

1 Introduction

Molecular calculations that employ the four-component Dirac–Coulomb or Dirac–Coulomb–Breit Hamiltonian have only recently become feasible [1, 2, 3, 4, 5]. The large computational demand that a four-component method makes is mostly due to the evaluation and handling of two-electron integrals that involve the small components of the wave function. Since these integrals contribute relatively little to the electronic energy it is appropriate to reduce their evaluation time by making judicious approximations. The simplest of these, complete neglect of an entire class of integrals, was considered in previous work [6] and has been remarkably successful in making larger calculations feasible. We now propose an extension of this method that further reduces the computational effort.

2 Method

We consider four-component calculations in which the upper and lower components of the four spinors are expanded in separate Gaussian type basis sets, $\left\{\left(\chi_\mu^{\mathrm{L}},0\right)^{\mathrm{T}}\right\},\left\{\left(0,\chi_\nu^{\mathrm{S}}\right)^{\mathrm{T}}\right\}$, that satisfy the kinetic balance condition

$$(\vec{\sigma}\cdot\vec{p})\chi_\mu^{\mathrm{L}} \in \{\chi^{\mathrm{S}}\}\forall\mu \ . \tag{1}$$

Expressed in terms of scalar functions the number of small-component basis functions, N^S, is about 3 times larger than the number of large-component functions, N^L. The matrix formulation of the Hartree–Fock problem is (in atomic units)

$$\begin{pmatrix} \mathbf{V}_N^{\mathrm{LL}}+\mathbf{J}^{\mathrm{LL}}-\mathbf{K}^{\mathrm{LL}} & c\Pi^{\mathrm{LS}}-\mathbf{K}^{\mathrm{LS}} \\ c\Pi^{\mathrm{SL}}-\mathbf{K}^{\mathrm{SL}} & \mathbf{V}_N^{\mathrm{SS}}+\mathbf{J}^{\mathrm{SS}}-\mathbf{K}^{\mathrm{SS}}-2c^2\mathbf{S}^{\mathrm{SS}} \end{pmatrix}\begin{pmatrix}\mathbf{C}_i^{\mathrm{L}}\\ \mathbf{C}_i^{\mathrm{S}}\end{pmatrix} = \begin{pmatrix}\mathbf{S}^{\mathrm{LL}} & 0\\ 0 & \mathbf{S}^{\mathrm{SS}}\end{pmatrix}\begin{pmatrix}\mathbf{C}_i^{\mathrm{L}}\\ \mathbf{C}_i^{\mathrm{S}}\end{pmatrix}\varepsilon_i \tag{2}$$

and solutions are found via a self-consistent-field procedure. The additional work that has to be done relative to a nonrelativistic Hartree-Fock calculation consists mainly of the evaluation of contributions to the operators **J** and **K** due to the small-component part of the wave function. It is therefore interesting to consider approximations that reduce this type of work, ideally to something that scales linearly with system size.

The first step is to analyze the relative importance of the different contributions to the Fock matrix, **F**. We start by breaking down all contributions to the matrix elements of Eq. (2) into products of integrals and density matrices. We note that the SL block is related to the LS block by the hermiticity of the Fock matrix and need not be considered separately. We explicitly label the M expansion centers of the basis function with a capital index (A, B, C, D) and indicate the number of large- and small- ($X=\mathrm{L/S}$) component functions that belong to this expansion center by $N^{X,A}$. Since these expansion centers coincide with the positions of the nuclei we can use the same labeling for the nuclear charge, Z. Individual matrix elements may then be labeled as

$$V_{N,\mu\nu}^{XX,\mathrm{AB}} = \sum_{\mathrm{C}}^{M}\int\frac{Z^{\mathrm{C}}}{r_C}\chi_\mu^{X,\mathrm{A}^\dagger}(\mathbf{r})\chi_\nu^{X,\mathrm{B}}(\mathbf{r})\mathrm{d}\mathbf{r} \ , \tag{3}$$

$$J_{\mu\nu}^{XX,\mathrm{AB}} = \sum_{\mathrm{C}}^{M}\sum_{\mathrm{D}}^{M}\left(\sum_{\kappa}^{N^{X,\mathrm{C}}}\sum_{\lambda}^{N^{X,\mathrm{D}}} D_{\lambda\kappa}^{XX,\mathrm{DC}}G_{\mu\nu,\kappa\lambda}^{XX,\mathrm{AB};XX,\mathrm{CD}} + \sum_{\kappa}^{N^{Y,\mathrm{C}}}\sum_{\lambda}^{N^{Y,\mathrm{D}}} D_{\lambda\kappa}^{YY,\mathrm{DC}}G_{\mu\nu,\kappa\lambda}^{XX,\mathrm{AB};YY,\mathrm{CD}}\right) \ , \tag{4}$$

$$K_{\mu\nu}^{XY,\mathrm{AB}} = \sum_{\mathrm{C}}^{M}\sum_{\mathrm{D}}^{M}\sum_{\kappa}^{N^{Y,\mathrm{C}}}\sum_{\lambda}^{N^{X,\mathrm{D}}} D_{\lambda\kappa}^{XY,\mathrm{DC}}G_{\mu\lambda,\kappa\nu}^{XX,\mathrm{AD};YY,\mathrm{CB}} \ , \tag{5}$$

$$\Pi_{\mu\nu}^{\mathrm{LS,AB}} = \int\chi_\mu^{\mathrm{L,A}^\dagger}(\mathbf{r})(\vec{\sigma}\cdot\vec{p})\chi_\nu^{\mathrm{S,B}}(\mathbf{r})\mathrm{d}\mathbf{r} \ , \tag{6}$$

with

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$$D_{\lambda\kappa}^{YX,\mathrm{DC}} = \sum_{i}^{\text{occ. spinors}} C_{\kappa,i}^{X,\mathrm{C}^*} C_{\lambda,i}^{Y,\mathrm{D}} \tag{7}$$

and

$$G_{\mu\nu,\kappa\lambda}^{XX,\mathrm{AB};YY,\mathrm{CD}} = \iint \frac{\chi_\mu^{X,\mathrm{A}^\dagger}(r_1)\chi_\nu^{X,\mathrm{B}}(r_1)\chi_\kappa^{Y,\mathrm{C}^\dagger}(r_2)\chi_\lambda^{Y,\mathrm{D}}(r_2)}{r_{12}} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \ . \tag{8}$$

Integrals of type $\mathbf{V}^{\mathrm{LL}}$ and $\mathbf{G}^{\mathrm{LL,\,LL}}$ are also required in a nonrelativistic calculation. We consider here the additional "relativistic" integrals. The two-index integrals $\mathbf{V}^{\mathrm{SS}}$, Π^{SL} and Π^{SL} are readily calculated since their number scales only quadratically with system size. The other terms show a quartic dependence on the number of basis functions and are responsible for the notorious computational bottleneck in four-component Hartree-Fock calculations. In Ref. [6] the neglect of all the contributions that arise from $\mathbf{G}^{\mathrm{SS,\,SS}}$ type integrals was considered. This rather crude approximation – that relies on the fact that their total contribution is small compared to other contributions in the SS block of the matrix – works surprisingly well. It suffices to add an a posteriori correction to the electronic energy to account for the neglected electron repulsion energy. The error in the wave function, even when probed with sensitive properties such as the electric field gradient on the nucleus [7], appears to be negligible.

The success of this simple method inspired us to explore this scheme further and to develop a new method that is computationally more efficient and possibly also numerically more accurate. The central idea is to rely on the localized nature of the small component of the wave function to systematically disregard all contributions to the potential-energy-matrix elements that involve small component integrals over functions with a different expansion center. In contrast to the old method we therefore do not disregard all $\mathbf{G}^{\mathrm{SS,\,SS}}$ type of integrals, but keep the pure one-center contributions. This should improve the screening of the nuclear potential and may thus give a more accurate wave function near the nuclei. The approximated integrals become

$${}^{1}\mathbf{G}^{\mathrm{SS,AB;LL,CD}} = \mathbf{G}^{\mathrm{SS,AB;LL,CD}}\delta_{\mathrm{AB}} \ , \tag{9}$$

$${}^{1}\mathbf{G}^{\mathrm{LL,AB;SS,CD}} = \mathbf{G}^{\mathrm{LL,AB;SS,CD}}\delta_{\mathrm{CD}} \ , \tag{10}$$

$${}^{1}\mathbf{G}^{\mathrm{SS,AB;SS,CD}} = \mathbf{G}^{\mathrm{SS,AB;SS,CD}}\delta_{\mathrm{AB}}\delta_{\mathrm{CD}} \ , \tag{11}$$

which reduces the computational scaling from quartic to cubic or quadratic. For consistency, we found it also necessary to apply the approximation to the two-index integrals as well:

$${}^{1}\mathbf{V}_N^{\mathrm{SS,AB}} = \mathbf{V}_N^{\mathrm{SS,AB}}\delta_{\mathrm{AB}} \ . \tag{12}$$

An obvious extension to the approximations just made is to make the secondary approximation

$${}^{2}\mathbf{G}^{\mathrm{SS,AB;SS,CD}} = \mathbf{G}^{\mathrm{SS,AB;SS,CD}}\delta_{\mathrm{AB}}\delta_{\mathrm{CD}}\delta_{\mathrm{AC}} \tag{13}$$

and to use the distance-dependent part of the simple Coulombic energy correction of Ref. [6] to correct the error due to the partial neglect of repulsion between core electrons on different atoms. We call the approximation defined by lines 9 to 12 method 1 and define method 2 as method 1 plus the secondary approximation (Eq. 13).

Let us consider the errors made when applying these approximation methods. The first error comes from the replacement of the full Coulomb potential,

$$V(\mathbf{r}) = \sum_{\mathrm{C}} \frac{Z^{\mathrm{C}}}{|\mathbf{r} - \mathbf{R}^{\mathrm{C}}|} - \sum_{i} \int \frac{\psi_i^{\mathrm{L}^\dagger}(\mathbf{r}_2)\psi_i^{\mathrm{L}}(\mathbf{r}_2) + \psi_i^{\mathrm{S}^\dagger}(\mathbf{r}_2)\psi_i^{\mathrm{S}}(\mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_2 \ , \tag{14}$$

by an approximated potential. The error is proportional to

$$V(\mathbf{r}) - {}^{1}V(\mathbf{r}) = -\sum_{\mathrm{A}} \sum_{\mathrm{B}\neq\mathrm{A}} \sum_{\mu}^{N^{\mathrm{S,A}}} \sum_{\nu}^{N^{\mathrm{S,B}}} D_{\nu\mu}^{\mathrm{SS,BA}} \int \frac{\chi_\mu^{\mathrm{S,A}^\dagger}(\mathbf{r}_2)\chi_\nu^{\mathrm{S,B}}(\mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_2 \ . \tag{15}$$

This error is due to the neglect of overlap between the small-component wave functions of atoms A and B. While this is certainly not a good approximation for the large-component part of the wave function it should work quite well for the small-component part that is both more localized and less affected by changes due to molecule formation.

Another error arises upon calculation of matrix elements over this potential. The error for matrix elements in the SS block is proportional to

$$\Delta\mathbf{F}_{\mu\nu}^{\mathrm{SS,AB}} = \int \chi_\mu^{\mathrm{S,A}^\dagger}(\mathbf{r})V(\mathbf{r})\chi_\nu^{\mathrm{S,B}}(\mathbf{r})\mathrm{d}\mathrm{A} \neq \mathrm{B} \ . \tag{16}$$

This term may become substantial for matrix elements that involve diffuse functions. Since the contribution to the energy is weighted by small-density matrix elements this should not affect the calculated electronic energy much. The problem is, however, that the erroneous matrix elements cause instabilities in the iterative Hartree-Fock procedure and unphysical positron orbital energies. In calculations we have seen variational collapse when only the approximations in Eqs. (9), (10), and (11) were applied. Simultaneous application of the approximation in Eq. (12) – i.e., making the full potential appear in Eq. (16) – prevented this behavior, although some energies in the positronic range turned out to be far too low. This is an artifact due to near-linear dependencies in the basis and is discussed later. The true error is roughly proportional to the value of the potential outside the core region (for matrix elements over diffuse functions) or is proportional to the overlap between core functions on different atoms (for matrix elements over tight functions). In both cases the errors are rather small.

Apart from these errors in the Coulomb part of the repulsion we also find errors in the nonlocal exchange terms. $\mathbf{K}^{\mathrm{LL}}$ is calculated exactly since it contains only contributions from the $\mathbf{G}^{\mathrm{LL,\,LL}}$ type integrals, but the other blocks are affected by the one-center approximation. We write the $\mathbf{K}^{\mathrm{SL}}$ block as

$$\begin{aligned} K_{\mu\nu}^{\mathrm{SL,AB}} &= \sum_{i}^{\text{occ. spinors}} \iint \frac{\chi_\mu^{\mathrm{S,A}^\dagger}(r_1)\psi_i^{\mathrm{S}}(r_1)\psi_i^{\mathrm{L}^\dagger}(r_2)\chi_\nu^{\mathrm{L,B}}(r_2)}{r_{12}} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \\ &= \sum_{i}^{\text{occ. spinors}} \sum_{\mathrm{D}}^{M} \sum_{\lambda}^{N^{\mathrm{S,D}}} C_{\lambda,i}^{\mathrm{S,D}} \iint \frac{\chi_\mu^{\mathrm{S,A}^\dagger}(r_1)\chi_\lambda^{\mathrm{S,D}}(r_1)\psi_i^{\mathrm{L}^\dagger}(r_2)\chi_\nu^{\mathrm{L,B}}(r_2)}{r_{12}} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \end{aligned} \tag{17}$$

and see that errors are weighted by the size of the molecular orbital (MO) coefficients. Again, we can expect small errors because we either have little overlap (tight functions) or a small value of the MO coefficient $\boldsymbol{C}^{\mathbf{S,D}}{}_{\lambda,\mathrm{i}}$ (diffuse functions). For the $\mathbf{K}^{\mathrm{SS}}$ block the same argument holds but the error should be even smaller in both absolute (because $\psi^{\mathrm{S}}{}_{\mathrm{i}}$ appears instead of $\psi^{\mathrm{L}}{}_{\mathrm{i}}$) and in relative sense (because the contribution is to the SS block that is dominated by the rest-mass energy).

On physical grounds we thus expect small errors caused by the approximations made in method 1. In practice we do, however, sometimes see significant errors, in particular, in the eigenvalue spectrum of the positron solutions. This can be related to the presence of near-linear dependencies in the basis set. The density matrix in the primitive nonorthogonal basis set is formed via a Löwdin back transformation of the matrix in the orthogonal basis set. Because small-component basis sets are quite dense it is not uncommon to find transformation coefficients of the order of a hundred or larger. For diffuse functions that have a large overlap with diffuse functions on another center, the transformation may cause dramatic magnification of relatively small errors in the nonorthogonal basis. This problem could, of course, be avoided by introducing a more sophisticated criterion for neglect of integrals that takes the actual overlap into account. A disadvantage is that introduction of a more sophisticated testing scheme may degrade the computational efficiency. Moreover investing effort in further tuning of the procedure is not very useful because the desired accuracy need not be high. We are concerned with the generation of a part of the potential that arises from less than 1% of the density (the first error discussed earlier) and by representing the full potential in matrix elements that are dominated by the $2c^2$ rest-mass term (the second error). In radon we have 0.63e or 0.7% of the charge in the small-component density; in neon this is only 0.03%. It suffices to correct artifacts due to near-linear dependencies to stabilize the Hartree-Fock self-consistent-field procedure. It turns out that this can be achieved by applying a simple projection method that does not affect the computational efficiency and simplicity of the original scheme. Refinements of this simple procedure could, if necessary, be taken into account when the computational scaling of the large-component or nonrelativistic part of the calculation is also tackled by introduction of more sophisticated approximate treatments.

The central idea in the projection method is to evaluate only one-center integrals over small-component functions to avoid the costly evaluation of multicenter integrals. The missing integrals should either be neglected or approximated by a sum of one-center integrals.

To find the expression in terms of one-center integrals we define the projection operator, **P**,

$$\mathbf{P}^{\mathrm{SS,AB}} = \left[\mathbf{S}^{\mathrm{SS,AA}}\right]^{-1}\mathbf{S}^{\mathrm{SS,AB}} \ , \tag{18}$$

which projects a small-component function on center B on the set of functions available on A:

$$\chi_{\nu}^{\mathrm{S,B}} \approx \mathrm{P}_{\mu\nu}^{\mathrm{SS,AB}}\chi_{\mu}^{\mathrm{S,A}} \ . \tag{19}$$

Neglected different multicenter integrals can then be taken into account by using the symmetric expression

$$\mathbf{G}^{\mathrm{AB;CD}} \approx \frac{1}{4}\Big\{\left[\mathbf{P}^{\dagger}\right]^{\mathrm{AB}}\left[\mathbf{P}^{\dagger}\right]^{\mathrm{CD}}\mathbf{G}^{\mathrm{BB,DD}} + \mathbf{G}^{\mathrm{AA,CC}}\mathbf{P}^{\mathrm{AB}}\mathbf{P}^{\mathrm{CD}} + \left[\mathbf{P}^{\dagger}\right]^{\mathrm{AB}}\mathbf{G}^{\mathrm{BB,CC}}\mathbf{P}^{\mathrm{CD}} + \left[\mathbf{P}^{\dagger}\right]^{\mathrm{CD}}\mathbf{G}^{\mathrm{AA,DD}}\mathbf{P}^{\mathrm{AB}}\Big\} \ . \tag{20}$$

Direct implementation of this formula saves integral-evaluation time but does not make the Fock matrix construction more efficient. In order to improve this step, we consider the Coulomb and exchange contributions separately. For evaluation of the Coulomb interaction the projection is broken down into two steps. The SS part of the density matrix is written as

$${}^{1}\mathbf{D}^{\mathrm{AA}} \approx \mathbf{D}^{\mathrm{AA}} + \frac{1}{2}\sum_{\mathrm{B}\neq\mathrm{A}}^{M}\left(\mathbf{D}^{\mathrm{AB}}\left[\mathbf{P}^{\dagger}\right]^{\mathrm{BA}} + \mathbf{P}^{\mathrm{AB}}\mathbf{D}^{\mathrm{BA}}\right) \tag{21}$$

to correct the error described in Eq. (15). This corrected density matrix is used to build an approximate Fock matrix that is block-diagonal in the expansion center label. The missing off-diagonal blocks are then generated according to

$$\mathbf{F}^{\mathrm{AB}} \approx \frac{1}{2}\left({}^{1}\mathbf{F}^{\mathrm{AA}}\mathbf{P}^{\mathrm{AB}} + \left[\mathbf{P}^{\dagger}\right]^{\mathrm{AB}}{}^{1}\mathbf{F}^{\mathrm{BB}}\right) \ . \tag{22}$$

This step reduces the error defined in Eq. (16). In both cases we see that the averaging of the left and right expanded matrices preserves the hermiticity of the Fock and density matrices, so use of permutational symmetry is still possible.

The error made in the exchange interaction requires a slightly different approach because this interaction cannot be factorized in the same manner as the Coulomb interaction. We chose the alternative expression

$$\mathbf{G}^{\mathrm{AD;CB}} \approx \left[\mathbf{P}^{\dagger}\right]^{\mathrm{CB}}\mathbf{G}^{\mathrm{AA;BB}}\mathbf{P}^{\mathrm{AD}} \tag{23}$$

to modify only the density matrix

$${}^{1}\mathbf{D}^{\mathrm{AB}} \approx \mathbf{D}^{\mathrm{AB}} + \mathbf{P}^{\mathrm{AD}}\mathbf{D}^{\mathrm{DC}}\left[\mathbf{P}^{\dagger}\right]^{\mathrm{CB}} \ . \tag{24}$$

The implementation of this procedure is simple with as major drawback the fact that the Coulomb and exchange parts of the Fock matrix need be evaluated separately owing to the difference in projected density matrices. This was not necessary in the original algorithm and gives a slight reduction in efficiency for small molecules. For larger molecules, separate treatment of exchange and Coulomb contributions is, however, more efficient because of improved screening of negligible contributions in the direct Hartree-Fock algorithm.

3 Applications

The methods described here were implemented in the DIRAC program system [8] by a minimal change of existing code. We chose three different model systems to test the validity of the approach. The most demanding test on the accuracy is to take two heavy elements that have a relatively short bond length. This means that two extensive basis sets are present and that we have significant small-component charges on both atoms. We took the CsAu molecule, for which reference results of Saue et al. [4] are available. On the other hand, we can take a large "nonrelativistic" system in which good accuracy should be easily reached but where the ideal computational scaling may be more difficult to achieve. We studied the computational scaling for varying lengths of polyacetylene chains. In between is the situation where one has a heavy atom close to a light molecule. As an example, a system of palladium and methane was chosen.

All the calculations were carried out on a 450 MHz Pentium III-based computer running under the Linux operating system. The convergence and screening thresholds were chosen such that accurate comparison of small energy differences was possible. In production runs these criteria could be relaxed, leading to more favorable timings, especially for the not approximated $\mathbf{G}^{\mathrm{LL,LL}}$ integral evaluations.

3.1 The CsAu molecule

The uncontracted Cs (23s17p10d1f) and Au (23s18p14d8f) basis sets of Saue et al. [4] were used. Small-component basis sets were generated via the restricted kinetic balance procedure. The geometry and harmonic frequency of the molecule were determined via a quadratic fit of five points spaced 0.01 Å around the minimum. The calculations were only done without the projection scheme.

The results displayed in Table 1 demonstrate that neglect of two-center integrals does not introduce large errors in either of the two methods. The decrease in total computational effort is modest because a relatively large amount of the $\mathbf{G}^{\mathrm{SS,LL}}$ integrals is still to be calculated. The effort involved in the calculation of the $\mathbf{G}^{\mathrm{SS,SS}}$ integrals – which dominated the computation time in earlier calculations – is, however, reduced significantly.

Table 1. Spectroscopic properties and computational efficiency of CsAu as calculated with the different schemes mentioned in the text

Method	R_e (Å)	D_e (kcal mol^{-1})	ω_e (cm^{-1})	Computation time (h)
Reference	3.412	−25.4413	78.80	17.5
1	3.413	−25.4259	78.77	11.3
2	3.413	−25.4253	78.77	9.0

3.2 Polyacetylene chains

The relativistically recontracted cc-pVDZ basis sets were used. These consist of (9s5p1d|3s2p1d) large-component basis sets for carbon and (4s1p|2s1p) for hydrogen. The contracted small-component basis sets generated via the unrestricted kinetic balance procedure consist of (5s10p5d1f|2s4p3d1f) for carbon and (1s4p1d|1s2p1d) for hydrogen, which clearly illustrates the strong increase in the number of basis functions in the relativistic domain. The geometry of the chains was fixed with a C–H bond length of 1.08 Å, C–C lengths of 1.45 Å, C=C lengths of 1.34 Å and bond angles of 120°. The errors in the calculated total energies are shown in Table 2.

The atomization energy of, for example, C_2H_4 was calculated to be 486 kcal mol^{-1}, so the errors are indeed very small. However, comparison with CsAu shows that the errors are larger, which is surprising because the constituting atoms are much lighter. This is due to the rather large near-linear-dependence effects in the small-component basis set. For the CsAu basis, we could use the restricted kinetic balance procedure since the basis set was left uncontracted. This was not possible for the contracted sets used for carbon and hydrogen, so the numerically less stable unrestricted kinetic balance procedure had to be used. Actually the observed pronounced deviations in especially the positronic levels stimulated us to derive and apply the projection method that was discussed previously. This scheme reduces the error in the positronic energies by orders of magnitude and also reduces the error in the total energy (that is solely determined by the electronic energy levels) by an order of magnitude. The remaining error should be sufficiently small for most practical purposes.

Table 2. Errors due to the approximation schemes in polyacetylene chains of varying lengths

Molecule	Without projection		With projection	
	Total energy (kcal mol^{-1})	Positronic orbital energy (au)	Total energy (kcal mol^{-1})	Positronic orbital energy (au)
C_2H_4	0.100	−22,271	−0.006	95
C_4H_6	0.218	−64,296	−0.002	169
C_6H_8	0.344	−164,324	0.017	270
C_8H_{10}	0.469	−289,668	0.043	380
$C_{10}H_{12}$	0.594	−447,673	0.069	459
$C_{12}H_{14}$	0.719	−588,564	0.095	544
$C_{14}H_{16}$	0.844	−722,984	0.122	545
$C_{16}H_{18}$	0.969	−844,892	0.148	655
$C_{18}H_{20}$	1.094	−940,619	0.174	692
$C_{20}H_{22}$	1.219	−1,012,264	0.201	718

The reduction in computational effort is apparent from the numbers in Table 3. Where the evaluation time of $\mathbf{G}^{SS,SS}$ integrals used to be the bottleneck, it becomes almost negligible in the different approximation schemes. The scaling of the timings with system size for method 2 is also displayed in Fig. 1, where we plot the computation time needed to evaluate the two-electron interaction as a function of system size (number of primitive basis functions). On the double-logarithmic plot one can see that the $\mathbf{G}^{SS,LL}$ integral evaluation initially exhibits cubic scaling with system size, as expected from Eq. (10), and levels off to quadratic as the system grows and conventional screening techniques take effect. The scaling of the $\mathbf{G}^{SS,SS}$ integral evaluation starts linear, in accordance with Eq. (13). At larger system size it dramatically increases to quartic behavior. The reason for this is that some initial steps in the integral evaluation have a quartic scaling with the number of basis functions shells and were not eliminated in the present implementation. Since the absolute timings are so small this is not really a problem.

3.3 Palladium and methane

For palladium, a contracted basis set (24s16p13d|7s6p6d) of K. Faegri Jr. (personal communication) was used. The small-component basis set (16s24p16d13f|5s8p6d6f) was generated via the unrestricted kinetic balance procedure. For carbon and hydrogen cc-pVTZ basis sets were used, consisting of (10s6p2d1f|4s3p2d1f) and (5s2p1d|3s2p1d) basis sets for carbon and hydrogen, respectively, in the large-components and the-small component basis sets (6s12p7d2f1g|3s6p5d2f1g) and (2s6p2d1f|2s4p2d1f) which were generated via the unrestricted kinetic balance procedure. The geometry was taken from the work of Diefenbach and Bickelhaupt [9] (geometry 1d in their Fig. 1). The calculations were only done without the projection scheme.

The results are displayed in Table 4 and demonstrate again that the neglect of two-center integrals does not introduce large errors in methods 1 and 2. The computational effort decreases significantly.

Table 3. Computation time (s) in each iteration as a function of system size for the polyacetylene chains for methods 1 and 2, for each of the integral classes $\mathbf{G}^{LL,LL}$ (LL), $\mathbf{G}^{SS,LL}$ (SL) and $\mathbf{G}^{SS,SS}$ (SS)

	LL	SL	SL (I)	SS	SS (I)	SS (II)
C_2H_4	4	29	7	90	5	1
C_4H_6	29	292	44	862	18	2
C_6H_8	114	1,177	128	3,331	43	4
C_8H_{10}	267	2,922	266	7,725	76	8
$C_{10}H_{12}$	486	5,437	454	13,817	122	15
$C_{12}H_{14}$	769	8,827	689	22,045	179	25
$C_{14}H_{16}$	1,123	12,834	980	31,544	255	40
$C_{16}H_{18}$	1,540	17,684	1,328	42,740	347	63
$C_{18}H_{20}$	2,026	23,266	1,731	55,439	455	94
$C_{20}H_{22}$	2,638	30,114	2,226	70,028	589	136

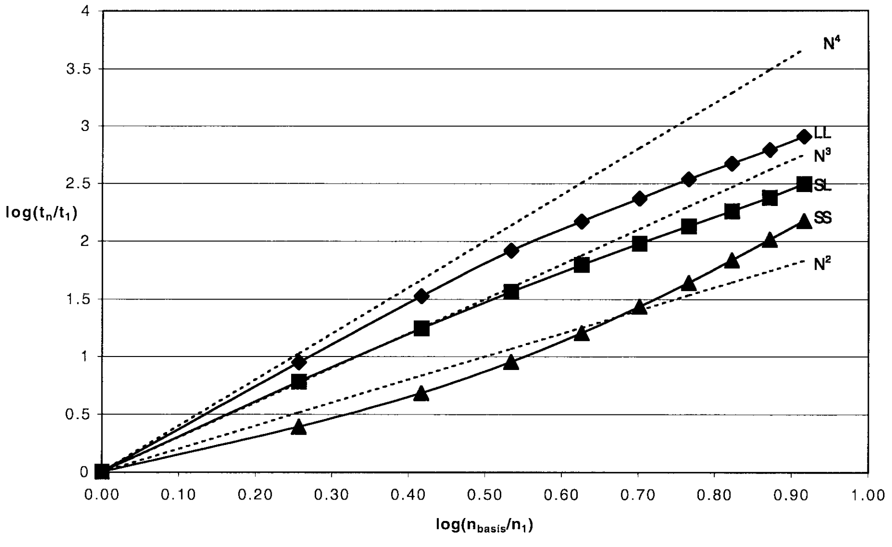

Fig. 1. Computation time used in integral evaluation and Fock matrix construction as a function of system size (number of primitive basis functions) for linear polyacetylene

Table 4. Error in total energy and computational efficiency for the Pd–CH_4 system as calculated with the different schemes mentioned in the text

Method	Error in total energy (kcal mol^{-1})	Computation time (h)
Reference	0	135.2
1	0.61	17.0
2	0.61	13.3

4 Conclusions

The computational effort of four-component molecular calculations can be greatly reduced by disregarding all integrals that involve small-component functions on different expansion centers. For three model systems, CsAu, polyacetylene chains, and a palladium–methane complex, it was shown that the errors due to the approximation are below chemical accuracy. Unphysically large errors that occurred in some cases were shown to be due to linear dependencies in the small-component basis and can be avoided by applying a simple projection method. The computational speed-up varied from a factor of 2 for CsAu to more than 20 for the largest polyacetylene chain.

The new method makes the Dirac–Hartree-Fock method applicable to large molecules. Generalization to four-component density functional theory is trivial and an implementation will probably become available in a new release of the DIRAC program system. Generalization to ab initio correlated calculations will also be considered in due course.

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