Basis Set Reduction in Hilbert Space

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We present Hilbert-space basis set reduction as a novel approach to reduce the computational effort of accurate correlation calculations for large basis sets. We motivate the method by an examination of the perturbative corrections in scaling theory and present a criterion for the choice of the internal basis. The method is illustrated with two calculations for the ground state of carbon and the energy curve of the beryllium dimer: In either case the errors introduced are less than 1% of the correlation energy. The method scales as the second power of the number of the basis functions and can exploit the benefits of massive parallelization.

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The calculation of many properties of atoms and molecules, in particular the ground-state energy, requires an accurate treatment of many-body effects. The many-body wave function is often expanded in Slater determinants constructed from a set of single-particle orbitals, i.e., from a finite and hence incomplete basis set. As the number of available orbitals (N) is increased the many-body wave function and energy converge *slowly* to their respective "complete-basis" values. At the same time the number of terms in the wave function and hence the computational cost increase, the methods currently used typically scale from N^4 to N^7 [1]. This very rapidly increasing cost is one of the chief limitations on our ability to perform accurate *ab initio* calculations for larger molecular systems. The slow convergence of the many-body energy with the number of single-particle orbitals N can be traced to the ansatz for the wave function: The electron-electron cusps in the wave function are poorly approximated by linear combinations of Slater determinants.

Many attempts have been made to improve the convergence of the many-body energy, for example, by including explicit correlation factors in the wave function [2]. Such methods trade a more compact form of the wave function for a more complex form of the Hamiltonian; i.e., the resulting many-body Hamiltonian is less sparse. Basis set reduction, as originally proposed by Freed [3], is an alternate approach to this problem: In Freed's method the majority of orbitals are treated in quasidegenerate many-body perturbation theory. The basis is partitioned in two distinct subsets of "internal" and "external" orbitals. Consider the internal subset of the basis as required describe the nonperturbative single-particle properties of the problem, i.e., the gross charge distribution of atom or molecule. The remaining external orbitals account for the contributions of the electron cusp in the many-body wave function and will be treated in an approximate fashion. We can then compute an effective Hamiltonian with only internal indices, which takes the effects of the external orbitals perturbatively into account. It is well known that the single-particle wave function and energy converge comparatively rapidly with the number of orbitals [4], therefore the internal subset constitutes only a small fraction of the full basis [5].

In the traditional approach, however, the effective Hamiltonian has to contain three-electron terms to achieve the desired accuracy [6]. These terms arise naturally even in first-order perturbation theory, and their number scales as N^6. As long as these terms are present it is difficult to obtain fundamentally faster convergence than traditional methods. In the method presented here the "effective Hamiltonian" for the internal basis is never explicitly constructed. We instead directly construct an approximate many-body state in the external space —shifting the focus from the construction of an explicit effective operator (Fock space) to the construction of an explicit many-body state (Hilbert space). Our main approximation is the neglect of the off-diagonal external many-body matrix elements [7]. We typically retain in excess of 99% of the total correlation energy, while maintaining the cost-advantage basis set reduction offers: Only a small subset of the total basis enters the expensive many-body calculation. The remaining "external" orbitals appear only in the basis-set-reduction step, which scales only as N^2 with the number of orbitals. The effects of the most important three-electron terms are taken into account, even though such terms never appear explicitly. The choice of internal basis as the minimal subset of the basis which requires nonperturbative techniques is nontrivial; we will return to it below.

We present the results for the ground state of carbon and the energy surface of the beryllium dimer. For carbon, Table I shows that our basis-set-reduction technique introduces errors consistently less than 1% of the contribution of the external orbitals to the energy, while the computational effort is reduced by about a factor of 10 compared to our implementation of a conventional method. The results for beryllium are particularly striking, since the equilibrium bond length depends crucially on the effects of the external orbitals (see Fig. 1). Using the internal basis sets alone we obtain only a poor description of the energy surface. The results from basis set reduction, however, closely approximate the exact en-

TABLE I. Basis-set-reduction errors (Δ^{BSR} in mH) and the number of "root" determinants (in parentheses) as a function of the threshold ϵ for the ^3P state of the carbon atom. The errors are defined as the energy difference between the basis-set-reduction result and the full CI energy of all orbitals. Three scenarios were considered: reduction from a QZP and TZP to an internal DZP basis, and reduction from the QZP basis to an internal TZP basis. In all cases the errors converge rapidly with ϵ to limiting values of less than 1% of the contribution of the external orbitals.

ϵ	$\Delta^{\text{BSR}}_{\text{TZP}\to\text{DZP}}$	$\Delta^{\text{BSR}}_{\text{QZP}\to\text{DZP}}$	$\Delta^{\text{BSR}}_{\text{QZP}\to\text{TZP}}$
5×10^{-2}	18.50 (12)	23.50 (10)	5.04 (12)
10^{-2}	1.51 (144)	1.80 (136)	1.57 (225)
5×10^{-3}	1.05 (202)	1.20 (230)	0.90 (462)
10^{-3}	0.33 (502)	0.63 (470)	0.12 (1529)
5×10^{-4}	0.27 (733)	0.56 (643)	
10^{-4}	0.21 (1155)	0.54 (865)	0.01 (8519)
5×10^{-5}	0.21 (1302)	0.53 (1218)	

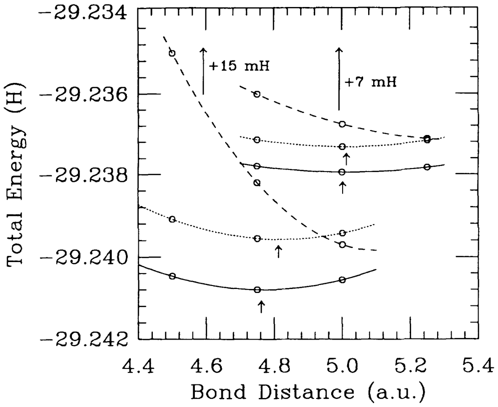

FIG. 1. Energy (H) of the beryllium dimer as a function of bond distance (a.u.). We investigated two basis sets (basis 2 and basis 5 from Harrison) with a total of 36 and 80 basis functions, respectively; the internal basis contains 22 functions in either case. Results for the large (small) basis are denoted by solid (open) symbols. We plot the FCI energy of the full basis (——), the HS-BSR energy (····), and the FCI energy of the internal basis (---). The latter were lowered by the indicated amounts to fit on the energy range in the graph. The full CI curve using all available orbitals shows a minimum, which is absent when only the internal orbitals are used to compute the energy. This minimum therefore stems entirely from effects of the external orbitals and is well reproduced in basis set reduction. The locations of the minima are indicated by arrows.

ergy curves.

We first compute the many-body state $\tilde{\Psi}_{\text{int}}=\sum a_i\Phi_i$ using only the Slater determinants Φ_i in the internal space. We use a full configuration interaction (CI) program [8] for this purpose, but any method which gives the coefficients of the many-body configurations may be employed [9]. We introduce a threshold parameter ϵ, select all determinants in $\tilde{\Psi}_{\text{int}}$ with large enough coefficients $|a|>\epsilon$ as "root determinants," and construct all single and double excitations from this set. For the kth external determinant Φ_k we then solve for the lower eigenvalue of

$$\begin{pmatrix} \langle\tilde{\Psi}_{\text{int}}|H|\tilde{\Psi}_{\text{int}}\rangle & \langle\Phi_k|H|\tilde{\Psi}_{\text{int}}\rangle \\ \langle\tilde{\Psi}_{\text{int}}|H|\Phi_k\rangle & \langle\Phi_k|H|\Phi_k\rangle \end{pmatrix}\begin{pmatrix}1\\ \alpha_k\end{pmatrix}=(\langle\tilde{\Psi}_{\text{int}}|H|\tilde{\Psi}_{\text{int}}\rangle\,\delta E_k)\begin{pmatrix}1\\ \alpha_k\end{pmatrix}, \tag{1}$$

and combine the coefficients α_k to form the state vector in the external space $\Psi^{\text{BSR}}_{\text{ext}}=\sum_k\alpha_k\Phi_k$. This external many-body state generates an effective field on the internal wave function. We finally solve for the variational wave function in the internal space [10] in the presence of this field, minimizing

$$E(\Psi^{\text{BSR}}_{\text{int}})=\langle\Psi^{\text{BSR}}_{\text{int}}|H|\Psi^{\text{BSR}}_{\text{int}}\rangle+(\langle\Psi^{\text{BSR}}_{\text{int}}|H|\Psi^{\text{BSR}}_{\text{ext}}\rangle+\text{H.c.})+\langle\Psi^{\text{BSR}}_{\text{ext}}|H|\Psi^{\text{BSR}}_{\text{ext}}\rangle\,. \tag{2}$$

These equations contain the two most important approximations in this theory: In Eq. (1) we have approximated the off-diagonal element by the matrix element between the external determinant and the internal state; an exact treatment would include coupling to the other external configurations. The variational degrees of freedom in Eq. (2) are restricted to the coefficients of the *internal* Slater determinants. We will argue below that this formulation recovers the most important contributions which arise in a scaling analysis (in momentum space) of the external energy contribution.

Since the internal many-body basis is a small fraction (often less than 1%) of the total many-body basis, this approach leads to a dramatic reduction in the computational effort in the variational step. Because external determinants are no longer coupled, the basis-set-reduction step scales as N_x^2 with the number of external orbitals N_x and is well suited for a massively parallel implementation. The vast majority of the matrix elements, namely, off-diagonal matrix elements involving more than two external indices, never enter the calculation and hence need not be computed in the four-index transformation preceding the correlation calculation.

We have investigated two cases to test the method. The results of our calculation for the ^3P state of *carbon* are shown in Table I. We investigated three basis sets, which were optimized by Dunning for the carbon atom [4]. (i) Basis 1: 14 orbitals, $(9s4p1d)/[3s2p1d]$, with 3 s orbitals, 2 p orbitals, and 1 d orbital. This basis set is labeled the double zeta basis (DZP) with d-wave polarization functions. The Hartree-Fock energy is essentially converged of this basis. (ii) Basis 2: 30 orbitals; in the triple zeta basis (TZP) $(10s5p2d1f)/[4s3p2d1f]$, one additional shell is added for each angular momentum, and one set of f-wave polarization orbitals is added. Using this basis set the full many-body [11] energy is lowered by 55.1 mH compared to basis 1. (iii) Basis 3: 55 orbitals; this set $(12s6p3d2f1g)/[5s4p3d2f1g]$ is the quadruple zeta basis (QZP) in the series. Compared with basis 2, the ground-state energy is lowered by 8.6 mH.

We present results for the basis-set-reduction error Δ^{BSR} for reduction from the QZP and TZP basis sets to an internal DZP basis and for reduction from the QZP basis to an internal TZP basis set. We define the basis-set-reduction error Δ^{BSR} as the difference between the full CI valence energy of the full basis and the energy obtained from basis set reduction. For each choice for the full and the internal basis we have varied the threshold parameter ϵ. We find that for sufficiently small thresholds ϵ, the errors saturate to values of less than 1% of the total external contribution. This accuracy is surprising, considering that up to 99.6% of the matrix elements of the many-body Hamiltonian have been neglected. To check that the error does *not* result from spurious cancellations, we verified that the angle between the exact external component of the wave function and its approximant is small ($\alpha \approx 0.08$). For most applications, the errors arising in the reduction to the smallest basis presented here should be tolerable. We have presented the results for reduction to an internal basis of triple zeta size to demonstrate that the accuracy of the result can be increased simply by increasing the size of the internal basis. The results also deteriorate when the internal basis is chosen too small: For reduction from a TZP to a minimal internal basis, the error increases to 66% of the total contribution.

The *beryllium dimer* is very weakly bound (see Fig. 1); determining the equilibrium bond distance has long been a challenge for quantum chemistry techniques [12]. Here we report results for basis 2 and basis 5 from Harrison and Handy [12], with a total of 36 and 80 basis functions, respectively. A large basis is required for an accurate description of this simple system, because the balance between the nuclear repulsion and the screening charge is very delicate. Beryllium does not bind in the Hartree-Fock approximation: The accurate treatment of correlation effects is therefore essential. In this light, the results from basis set reduction are particularly striking: For the small basis, using the internal orbitals alone (11 orbitals per atom; see the dashed lines in Fig. 1) we find no minimum for bond length from 4.5 to 5.25 a.u. Nevertheless the basis-set-reduction energies (dotted lines) are essentially parallel to the full CI curve (solid lines), which was taken from the calculation of Harrison and Handy [12]. We further note that the relative errors in the energy differences between the points are only about 10%. This indicates that energy differences are reproduced to within a small fraction of the absolute basis-set-reduction error; the minima of the potential curves are virtually identical. For the large basis, where the number of external orbitals is increased almost fourfold, the minima shift by about 0.3 a.u. This shift is again faithfully reproduced by the basis-set-reduction result, which has a minimum at 4.82 a.u. while the full CI minimum is at 4.77 a.u. Only the most expensive traditional techniques render bond length of comparable quality. The fact that basis set reduction is capable of capturing these effects instills some confidence that this method can accurately treat the correlation effects in the external basis for other multireference molecular calculations.

Scaling theory.— We briefly digress to perturbation theory to compare the energy contributions of the external orbitals as they arise in momentum-space scaling theory and in basis set reduction: If we assume that the Hartree-Fock energy is essentially converged for the internal basis, the many-body configurations with external orbitals will mainly contribute to the description of the electron-electron cusps in the wave function. It is known that wave functions with momenta of order p yield contributions of order $\Delta E(p) \sim p^{-3}$ to the correlation energy [2]. We note that for the basis sets discussed here, the momenta of the external orbitals are at least about 4 times larger than the momenta of the valence orbitals. For basis set reduction to succeed, we must therefore recover the contributions of the orbitals with high momenta in our formalism. It can be shown that the only correction of order p^{-3} arises in first order in perturbation theory from double excitations into external orbitals. If we expand the coefficients in the external state in Eq. (1) to first order, we recover exactly the same term. Terms which involve matrix elements between two different external configurations first arise in second order and are suppressed by a factor of $O(p^{-2})$ with respect to the leading term [13].

Choice of the internal basis.— The poor results for large threshold ϵ, i.e., few internal "root" determinants, and for small internal basis sets indicate that care must be exercised in the choice of the internal basis. The scaling analysis of the external contributions suggests that this formalism is well suited to incorporate the high-momentum corrections to the electron-electron cusps in the wave function. To obtain the leading correction we must accurately treat double excitations into external space. If the "single-particle" properties of the system are *not* adequately described by the internal basis, external orbitals contribute significantly to the occupied molecular orbitals. This means that Slater determinants with three external orbitals will become important in the many-body state; the extra excitation level arises from the unitary transformation to the molecular orbitals. Such triple excitations are not included in the wave function constructed by our method; it is therefore not surprising that it fails when the internal basis is chosen too small. We must therefore require that the Hartree-Fock energy is well converged on the internal basis [13]; an internal double zeta basis is usually sufficient.

In conclusion, basis set reduction in Hilbert space leads to a dramatic reduction of the computational effort in accurate atomic and molecular calculations with standard basis sets. The computational effort to treat the external orbitals is ultimately dominated by the four-index transformation on the external indices, even when we take advantage of the fact that off-diagonal integrals with more than two external indices do not appear in the calculation. We would like to point out that there is no requirement that Hartree-Fock orbitals be used for the external orbitals. This offers the opportunity to localize the external orbitals for large molecules, using any of the standard techniques [14]. Generalizing the method presented here, we may be able to construct an *ab initio* pseudopotential for the core electrons in heavy elements for the treatment of core-valence correlation corrections.

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[1] For a recent introductory overview of the field and the methods discussed in this paper, see, for example, A. Szabo and Neil S. Ostlund, *Modern Quantum Chemistry* (McGraw-Hill, New York, 1989); W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley, New York, 1986).

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[3] K. F. Freed, Acc. Chem. Res. **16**, 137 (1983).

[4] T. H. Dunning, J. Chem. Phys. **90**, 1007 (1988).

[5] Typically we choose a subset of the molecular orbitals of double zeta size as the internal basis. The remaining basis functions constitute the external basis.

[6] X. Wang and K. F. Freed, J. Chem. Phys. **91**, 1142 (1989).

[7] Such approximations may have been considered previously for smaller internal basis sets. We believe that if the internal subset of the basis fails to converge the SCF wave function, the approximate treatment of the external states is not sufficiently accurate. The method presented here cannot both improve the Hartree-Fock wave function *and* account for accurate correlation corrections at the same time.

[8] To solve the full CI equations in this fashion we have to solve the generalized eigenvalue problem in the space spanned by Ψ and an individual determinant Φ. This method is closely related to the method of optimal relaxation; see I. Shavitt, C. F. Bender, A. Pipano, and R. P. Hosteney, J. Comput. Physics **11**, 90 (1973).

[9] K. G. Wilson and W. Wenzel, "State Selection in the Configuration Interaction Method" (unpublished).

[10] This typically requires one more iteration in the CI procedure for the internal basis.

[11] All calculations were done in the frozen-core approximation.

[12] R. J. Harrison and N. C. Handy, Chem. Phys. Lett. **98**, 97 (1983), and references therein.

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