

## Fast localized orthonormal virtual orbitals which depend smoothly on nuclear coordinates

Joseph E. Subotnik,<sup>a)</sup> Anthony D. Dutoi,<sup>b)</sup> and Martin Head-Gordon<sup>c)</sup>

*Department of Chemistry, University of California, Berkeley, California 94720 and  
Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720*

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We present here an algorithm for computing stable, well-defined localized orthonormal virtual orbitals which depend smoothly on nuclear coordinates. The algorithm is very fast, limited only by diagonalization of two matrices with dimension the size of the number of virtual orbitals. Furthermore, we require no more than quadratic (in the number of electrons) storage. The basic premise behind our algorithm is that one can decompose any given atomic-orbital (AO) vector space as a minimal basis space (which includes the occupied and valence virtual spaces) and a hard-virtual (HV) space (which includes everything else). The valence virtual space localizes easily with standard methods, while the hard-virtual space is constructed to be atom centered and automatically local. The orbitals presented here may be computed almost as quickly as projecting the AO basis onto the virtual space and are almost as local (according to orbital variance), while our orbitals are orthonormal (rather than redundant and nonorthogonal). We expect this algorithm to find use in local-correlation methods. © 2005 American Institute of Physics. [DOI: 10.1063/1.2033687]

### I. INTRODUCTION

The role of localized molecular orbitals has long been understood as crucial in computational quantum chemistry. From a physical perspective, localized orthonormal occupied orbitals demonstrate the intuitive bonding between atoms and most work today on localized orbitals has focused on the occupied space. In a paper published more than 50 years ago,<sup>1</sup> Lennard-Jones and Pople first conceived of localized occupied orbitals as physically meaningful mathematical constructions that maximized local symmetry. A decade later, Boys proposed localizing orbitals by minimizing the product of variances of the orbitals, a novel idea which was limited only by the computational difficulty it presented.<sup>2</sup> In 1963, however, Edmiston and Ruedenberg demonstrated the first viable algorithm for computing localized orbitals.<sup>3</sup> Edmiston and Ruedenberg (ER) proposed localizing occupied orbitals by maximizing the self-interaction of a collection of orbitals across all different rotations. They also proposed minimizing the sum of the variances of the localized orbitals, which was a modification of the Boys' function and which is the foundation for what are today known as (and what we shall call) Boys orbitals.<sup>4</sup>

$$\zeta_{\text{Boys}}(\chi_1, \dots, \chi_N) = \sum_{i=1}^N \langle \chi_i | (r - \langle \chi_i | r | \chi_i \rangle)^2 | \chi_i \rangle, \quad (1)$$

$$\zeta_{\text{ER}}(\chi_1, \dots, \chi_N) = \sum_{i=1}^N \langle \chi_i | \chi_i | \frac{1}{r} | \chi_i \chi_i \rangle. \quad (2)$$

These localization models of Edmiston and Ruedenberg were very successful both because they gave well-localized, physically meaningful occupied orbitals and because the proposed method for computing localized orbitals (by taking Jacobi sweeps) allowed fast convergence.

Since the seminal ER paper of 1963, more theoretical chemists (including Pipek and Mezey<sup>5</sup>) have proposed new and different schemes for finding localized orthonormal occupied orbitals, hoping to find both more physically meaningful orbitals and computationally cheaper orbitals. Today, Boys, ER, and Pipek-Mezey orbitals are the three principal orbitals used by computational chemists to compute localized orthonormal occupied orbitals. Judged by their physical nature, the Pipek-Mezey and ER orbitals are more physical than the Boys orbitals, for they preserve  $\sigma$ - $\pi$  separation (e.g., in benzene).<sup>5</sup> Judged by speed, however, the Pipek-Mezey and Boys orbitals are much faster to compute than the ER orbitals. For large systems that can be tackled with today's computer power, the speed of orbital calculation is essential; computing orbitals should not take longer than the subsequent electron correlation calculations.

The key ingredient which allows fast computation of localized occupied orbitals via the three localization techniques above is that all three localization functions usually have strong and isolated minima. This allows most optimization techniques [e.g., Jacobi sweeps, conjugate gradient, and Broyden-Fletcher-Goldfarb-Shanno algorithm (BFGS)] to converge rapidly to stationary points.<sup>3,6,7</sup>

For the virtual space, by contrast, optimization of localization functions does not converge rapidly to a minimum. Convergence is slow and painful. There appear to be many local minima, and these are not well separated.

Furthermore, besides computational difficulties, there are also intrinsic theoretical difficulties to the idea of local-

<sup>a)</sup>Electronic mail: subotnik@berkeley.edu

<sup>b)</sup>Electronic mail: t\_dutoi@bastille.cchem.berkeley.edu

<sup>c)</sup>Electronic mail: mhg@cchem.berkeley.edu

izing the space of virtual orbitals. For example, as the atomic-orbital (AO) basis grows for one molecule, the AO set may become linearly dependent. This would obviously make orthonormal localization impossible. Furthermore, in the limit of an infinite linearly independent AO basis, the most local orthonormal basis for the virtual space would be a set of delta functions, which are jagged functions. Intuitively, we then expect the isosurfaces of any localizing function to also become more jagged. We hypothesize, therefore, that convergence will be more and more difficult if we insist on optimizing a localization function over the virtual space.

Moreover, often in chemistry, one seeks to create a smooth potential-energy surface for a molecule along a reaction coordinate. For traditional self-consistent-field (SCF) and correlation methods, which are invariant to transformations of the occupied (and virtual) functions amongst themselves, the smoothness of potential curves is guaranteed within a given AO basis. But local-correlation methods break such invariances, meaning that one must explicitly require not only that the localized occupied and virtual orbitals be well defined but also that they be smooth functions of the nuclear coordinates. This stipulation makes impossible the use of traditional localization functions in order to localize virtual orbitals, for as basis size grows and localization functions take on multiple nonisolated minima, finding one stationary point that changes smoothly with nuclear position seems impossible.

For all of these reasons, localized orthonormal orbitals are today primarily restricted to the occupied space, ignoring the virtual space (though there are a few notable exceptions<sup>8</sup>). This is an unfortunate reality. Modern local-correlation techniques<sup>9-13</sup> would certainly benefit from a stable algorithm that produced local orthonormal virtual orbitals. In traditional CCSD or MP2, for example, one encounters amplitudes of the form  $t_{ij}^{ab}$ , where  $i, j$  are orthonormal occupied orbitals and  $a, b$  are orthonormal virtual orbitals. When the virtual orbitals are strongly localized just as the occupied orbitals are, one can invoke the sparsity of the  $t$ -vector and speed up a calculation with little loss of accuracy, using simple equations designed for orthonormal orbitals.<sup>14</sup>

In the absence of maximally localized, smooth, orthonormal virtual orbitals, computational chemists have adapted to using local redundant sets of orbitals spanning the virtual space. For example, the standard local-correlation techniques descended from Saebo and Pulay<sup>9</sup> to Werner and co-workers<sup>10,11</sup> employ localized, orthonormal occupied orbitals and a redundant basis for the virtual space formed by projecting the AO basis onto the virtual space. Seeking to avoid the use of redundant orbitals, we present here an algorithm which avoids optimization of any localizing function, invoking only the locality of the AO basis to produce well-defined, localized, orthonormal virtual orbitals that depend smoothly on nuclear position. As of the publication of this paper, we do not know of any stable method which generates such orbitals.

## II. OUR ALGORITHM

### A. Notation

Before discussing our algorithm further, we want to define our variables. For the rest of this paper, we use the following notational conventions:  $N$  is the number of basis functions in a calculation,  $N_A$  is the number of atoms in our molecule,  $N^{(a)}$  is the number of atomic orbitals for atom  $a$ ,  $N_M^{(a)}$  is the minimal number of atomic orbitals for atom  $a$  (1 or 5 for light atoms),  $N_{\text{HV}}^{(a)}$  is the number of hard-virtual (HV) orbitals for atom  $a$ :  $N_{\text{HV}}^{(a)} = N^{(a)} - N_M^{(a)}$ ,  $|\chi_i^{(a)}\rangle$  is the  $i$ th atomic orbital attached to atom  $a$ , and  $|\sigma_i^{(a)}\rangle$  is the  $i$ th ‘‘proto-HV’’ orbital on atom  $a$ . This will be defined shortly.

An orbital or constant is atom independent without the ( $a$ ) superscript. For example,

$$N = \sum_{a=1}^{N_A} N^{(a)}. \quad (3)$$

### B. Philosophy

The basic premise of our algorithm is that one may partition the entire AO vector space  $A$  into a minimal basis space  $E$  (which exactly includes the occupied space  $O$ ) and a set of atom-labeled extravalence or hard virtuals ( $H$ ) which include polarization, diffuse, and higher harmonic functions, i.e., orbitals that are not largely represented in the SCF solution for the molecule. Formally, we postulate that

$$A = E \oplus H,$$

where we can construct automatically an atom-centered localized basis for  $H$  with little effort. Furthermore, if we decompose the minimal basis space into the occupied space  $O$  and the valence virtual space  $L$ , we expect that standard localization schemes (e.g., Boys, ER, or Pipek-Mezey) should find strong, isolated maxima over  $L$  and  $O$  representing unique, smoothly varying localized orthonormal orbitals. We expect this to be so because both the valence virtual space and the occupied space are chemically meaningful (unlike the hard-virtual space), as can be demonstrated by perfect-pairing algorithms.<sup>15-22</sup> Our final decomposition is

$$A = O \oplus L \oplus H,$$

where we produce a local, atom-centered basis for  $H$  and do standard localization on  $L$ . Here  $O \perp L \perp H$ .

We mention now two pieces of insight that underlie our approach and allow our algorithm to succeed. First, we note that for any given atom, in any molecular geometry and regardless of the details of the occupied space, the AO vector space attached to that atom should decompose roughly into two subspaces: one subspace associated with the molecule’s minimal basis space and another subspace associated with the hard virtuals for that atom. The implication is that one can project out a *molecule’s* minimal basis space from the AO space on a single *atom* and end up with the hard-virtual space on that *atom*. This will be made precise below. This view of a minimal basis owes its roots to many chemists, including Mulliken,<sup>23</sup> Davidson,<sup>24</sup> Roby,<sup>25</sup> Ahlrichs and co-workers,<sup>26,27</sup> Ruedenberg and co-workers,<sup>28-31</sup> Reed

*et al.*,<sup>32</sup> Mayer,<sup>33,34</sup> and Lee and Head-Gordon.<sup>35,36</sup>

Second, we remind the reader that, before ever doing a single calculation on a given molecule, one can *a priori* make an educated guess as to what the hard virtuals look like. Again, by definition, the hard virtuals are atom-centered orbitals formed by taking the full AO basis  $A$  and subtracting off the minimal basis space. Thus, to a good approximation, the hard virtuals for one atom are the AO basis for that atom minus the minimal basis for that atom. Now, one can estimate the minimal basis for an atom as simply the atomic orbitals of the free atom [as represented by a standard minimal basis such as Slater-type orbital (STO)-3G]. Accordingly, with just simple projection operations, one may guess a set of “protohard-virtual orbitals” (or proto-HV’s) for any given atom in any molecular geometry, and hence one has proto-HV’s for the entire molecule. The magic here is that, armed with  $N-N_M$  proto-HV’s, we can rotate any other given set of  $N-N_M$  vectors so that they most resemble the proto-HV’s. (This can be done with a simple formula in one step as demonstrated in Refs. 37 and 38.) These proto-HV’s can thus help us find tightly localized orbitals without optimization of any defining function.

Before going into any algorithmic details, let us provide a chemical example which should provide intuition and motivation for the algorithm that follows. Consider the diatomic molecule  $N_2$  at equilibrium geometry in a 6-31G\* basis, where the size of the total AO basis is 30 functions, with 15 on each N atom. For each N atom, these 15 functions may be divided into 1  $s$  shell (1 function), 2  $sp$  shells (8 functions), and 1 Cartesian  $d$  shell (6 functions). Now, we focus on the spin-up orbitals. The occupied space has dimension 7, and we propose that we can find a minimal basis space of dimension 10 which exactly includes the occupied space. This minimal basis space should resemble the STO-3G space for  $N_2$  (i.e., contain large  $\{1s, 2s, 2p_x, 2p_y, \text{ and } 2p_z\}$  contributions around each atom). Accordingly, the valence virtual space will have dimension 3 and be made mostly of contributions from the  $p$  orbitals on the N atoms. Finally, we propose that we can find 10 additional virtual orbitals for each N atom roughly by taking the AO basis for that atom and projecting out the minimal basis space; these hard-virtual functions will look like 1  $sp$  shell (4 functions) and 1 Cartesian  $d$  shell (6 functions). By this, we have constructed 23 localized orthonormal virtual orbitals.

## C. Algorithmic details

### 1. The protohard-virtual orbitals

The first step in our algorithm is the construction of the proto-HV’s. This needs to be done once for each basis (i.e., 6-31G\*, cc-pVDZ, etc.) for every type of atom (i.e., N, C, etc.). Furthermore, we do this for every angular momentum and component separately. For concreteness, let us focus on the three  $s$  orbitals for C in a 6-31G basis. Let  $\{\phi_i\}$  be an orthonormal basis for the C atom in a 6-31G basis. We first project the two STO-3G  $s$  orbitals into the 6-31G  $s$  orbital space.

$$|\xi_j^s\rangle = \left( \sum_{i=1}^3 |\phi_i^s\rangle\langle\phi_i^s| \right) |\chi_j^{\text{STO-3G},s}\rangle, \quad j = 1, 2. \quad (4)$$

We then orthonormalize the set  $\{\xi_j^s\}$ , resulting in new vectors  $\{\eta_j^s\}$ . At this point, we project out all components of this  $\eta$  space from the 6-31G basis and form the new overlap matrix.

$$|\psi_j^s\rangle = \left( \text{Id} - \sum_{i=1}^2 |\eta_i^s\rangle\langle\eta_i^s| \right) |\chi_j^{6-31G,s}\rangle, \quad j = 1, 2, 3. \quad (5)$$

$$S_{ij} = \langle\psi_i^s|\psi_j^s\rangle. \quad (6)$$

Finally, we diagonalize  $\mathbf{S} = \mathbf{U}\mathbf{\Lambda}\mathbf{U}^T$ . For the case at hand,  $\mathbf{S}$  has two eigenvalues that are zero, and we consider the vector corresponding to the nonzero eigenvalues.

$$|\sigma_i^s\rangle = \sum_j |\psi_j^s\rangle U_{ji}, \quad i > 2. \quad (7)$$

At last, we have our proto-HV space, which is spanned by  $\{\sigma_i^s\}$ . For the  $s$  part of 6-31G, there is only one vector in this space and we are done. In a bigger basis, to complete this process, we would now perform ER optimization on all of the  $\{\sigma_i^s\}$  in order to separate the proto-HV’s into a shell-like structure.

This process is repeated for each higher angular momentum ( $p$  and  $d$  in 6-31G) and is done for every atom type in our molecule. In the end, the span of  $\{\sigma_i\}$  is our guess at the entire hard-virtual space for our molecule. Note that every proto-HV has a preassigned angular momentum.

### 2. The minimal basis space $E$

Our algorithm next performs a SCF calculation, followed by the creation of a minimal basis space ( $E$ ) for the molecule that exactly includes the occupied space. Many possibilities present themselves for how we may build  $E$ . One might, for instance, use the Extracted Polarized Atomic Orbital (EPAO) space construction of Lee and Head-Gordon *et al.*<sup>36</sup>

For our calculations, we have chosen to come back to the STO-3G vector space and again use various projections and overlap matrices for consistency with the procedure above. Let us assume we are working in a 6-31G basis and let  $\{\phi_i\}$  be an orthonormal basis for the 6-31G basis for our molecule. First, we project the STO-3G basis for our molecule into the 6-31G AO basis.

$$|\xi_j\rangle = \left( \sum_i^{N_{6-31G}} |\phi_i\rangle\langle\phi_i| \right) |\chi_j^{\text{STO-3G}}\rangle, \quad j = 1, \dots, N_{\text{STO-3G}} = N_M. \quad (8)$$

Now, let  $\{e_1, \dots, e_{N_o}\}$  be an orthonormal basis for the occupied space in our 6-31G calculation. At this point, we project out all components of the occupied space from the  $\xi$  space and form the new overlap matrix.

$$|\psi_j\rangle = \left( \text{Id} - \sum_{i=1}^{N_o} |e_i\rangle\langle e_i| \right) |\xi_j\rangle, \quad j = 1, \dots, N_M, \quad (9)$$



$$S_{ij} = \langle \psi_i | \psi_j \rangle. \quad (10)$$

We then diagonalize  $\mathbf{S} = \mathbf{U}\mathbf{\Lambda}\mathbf{U}^T$ . If  $N_o$  is the number of occupied orbitals, we hope that  $\mathbf{S}$  has  $N_o$  eigenvalues that are close to zero. We consider the vectors corresponding to the largest eigenvalues,

$$|e_i\rangle = \sum_{j=1}^{N_M} |\psi_j\rangle U_{ji}, \quad i = N_o + 1, \dots, N_M. \quad (11)$$

We now *define* the vectors  $\{e_{N_o+1}, \dots, e_{N_M}\}$  to be a basis for our valence virtual space of our molecule. We define our minimal basis space to be the span of  $\{e_1, \dots, e_{N_o}, e_{N_o+1}, \dots, e_{N_M}\}$ .

Lastly, we localize the virtual valence space (and, for parallelism, the occupied space as well) with the Boys algorithm. We denote the resulting Boys-localized occupied orbitals  $\{\tilde{e}_1, \dots, \tilde{e}_{N_o}\}$  and the resulting Boys-localized valence virtual orbitals  $\{\tilde{e}_{N_o+1}, \dots, \tilde{e}_{N_M}\}$ . At last, we have completely specified a set of localized orthonormal orbitals  $\{\tilde{e}_1, \dots, \tilde{e}_{N_M}\}$  which span a minimal basis space ( $E$ ) and function as a simpler, noniterative alternative to the EPAO's of Lee and Head-Gordon.

### 3. The hard virtuals

The final piece of our algorithm is the construction of the hard virtuals. We begin our calculation by projecting all of the atomic orbitals for each atom into  $H$ , the orthogonal complement of the minimal basis space  $E$ .

$$|\eta_j^{(a)}\rangle = \left( I - \sum_{i=1}^{N_M} |e_i\rangle\langle e_i| \right) |\chi_j^{(a)}\rangle, \quad j = 1, \dots, N^{(a)}. \quad (12)$$

From this collection, we generate  $N_{\text{HV}}^{(a)}$  linearly independent vectors by forming and diagonalizing the overlap matrix

$$S_{ij}^{(a)} = \langle \eta_i^{(a)} | \eta_j^{(a)} \rangle, \quad \mathbf{S}^{(a)} = \mathbf{U}^{(a)} \mathbf{\Lambda}^{(a)} (\mathbf{U}^{(a)})^T. \quad (13)$$

This is the trickiest part of our algorithm. Just as when we constructed the space  $E$  above, we hope that, among the eigenvalues of  $S^{(a)}$ , we have  $\lambda_{N_M^{(a)}} \ll \lambda_{N_M^{(a)}+1}$ . The details behind this crucial assumption will be discussed later. Ideally, we would hope  $\lambda_{N_M^{(a)}} \approx 0$  and  $\lambda_{N_M^{(a)}+1} \approx 1$ . These can be exact equalities in the limit of a one-atom system only. We keep those eigenvectors which correspond only to the biggest eigenvalues

$$|\xi_j^{(a)}\rangle = \sum_{k=1}^{N^{(a)}} |\eta_k^{(a)}\rangle U_{kj}, \quad j = N_M^{(a)} + 1, \dots, N^{(a)}. \quad (14)$$

At this state, every atom has an associated collection of nonorthogonal but linearly independent vectors. For each atom, we orthogonalize and then tighten this collection by rotating it towards the position of maximal overlap with the proto-HV's discussed above and in Ref. 37. Formally, if we let

$$\mathbf{R}_{ij}^{(a)} = \langle \xi_i^{(a)} | \xi_j^{(a)} \rangle, \quad \mathbf{T}_{ij}^{(a)} = \langle \xi_i^{(a)} | \sigma_j^{(a)} \rangle, \quad (15)$$

then the new set of orbitals is constructed as<sup>39</sup>

$$\mathbf{Z}^{(a)} = (\mathbf{R}^{(a)})^{-1} \mathbf{T}^{(a)} ((\mathbf{T}^{(a)})^T (\mathbf{R}^{(a)})^{-1} \mathbf{T}^{(a)})^{-1/2}, \quad (16)$$

$$|\gamma_i^{(a)}\rangle = \sum_{j=1}^{N^{(a)}} |\xi_j^{(a)}\rangle Z_{ji}^{(a)}. \quad (17)$$

Finally, every atom has an associated collection of well-defined, linearly independent orbitals, which are orthonormal relative to each other, but which are not orthonormal relative to the orbitals on different atoms. In order to make the full set of hard virtuals orthogonal, one option is to perform symmetric orthogonalization on this space.

$$S_{ij} = \langle \gamma_i | \gamma_j \rangle, \quad \mathbf{W} = \mathbf{S}^{-1/2}, \quad |h_i\rangle = \sum_{j=1}^{N_{\text{HV}}} |\gamma_j\rangle W_{ji}. \quad (18)$$

This last step, however, is not optimal. Symmetric orthogonalization treats all orbitals equivalently, meaning that a tight  $s$  polarization function on atom 1 will gain a piece of a diffuse hard virtual on atom 2. A better alternative is to separate all of the hard virtuals on different atoms into "importance classes," with tight functions in one class and diffuse functions in another. Then one may first perform symmetric orthogonalization on all tight virtual functions to orthogonalize between different atomic collections. Subsequently, one projects this tight space out of the remaining diffuse space, retightens the diffuse functions to their proto-HV's as above, and finally then performs symmetric orthogonalization to orthogonalize between collections of diffuse hard virtuals on different atoms. This procedure can be carried out with an arbitrary number of importance classes defined at the beginning of the program.

### D. A sketch of the code

For completeness, we now summarize the procedure above briefly as follows:

- (1) Construct the proto-HV's for our vector space.
- (2) Form the valence virtual space ( $L$ ) and the minimal basis space  $E$ .  $E = L \oplus O$ . Call  $H$  the orthogonal complement of  $E$  in the AO vector space.
- (3) Localize the valence virtual space with the Boys algorithm.
- (4) Loop over atoms  $a$ . Let  $W_a$  be the set of AO's attached to atom  $a$ . As always,  $N^{(a)}$  is the size of  $W_a$  and  $N_M^{(a)}$  is the size of the minimal basis for atom  $a$ .
  - (a) Project  $W_a$  onto  $H$ . Call this new set of vectors  $\tilde{W}_a$ .
  - (b) Form the overlap matrix  $\tilde{S}_a$  of  $\tilde{W}_a$ .
  - (c) Diagonalize  $\tilde{S}_a$  and keep only the  $N^{(a)} - N_M^{(a)}$  eigenvectors which correspond to the  $N^{(a)} - N_M^{(a)}$  largest eigenvalues. We presume that there should be  $N_M^{(a)}$  eigenvalues close to zero. Call this new set of vectors  $Y_a$ .
- (5) Loop over importance groups  $i$  for the HV space. We propose that there should be two such groups here:  $i = 1$  (nondiffuse) and 2 (diffuse).
  - (a) Let  $T^i$  be a list of all orbitals with importance  $i$ . Initialize  $T^i = \{\emptyset\}$ .
  - (b) Loop over atoms  $a$ .

- (i) Apply the most-resembling function [Eqs. (16) and (17)] matching the set  $Y_a$  to its proto-HV's.
- (ii) Extract the orbitals from  $Y_a$  which correspond to importance group  $i$ . Call these orbitals  $Y_a^i$ . Add them to the list  $T^i$ .
- (c) Compute the overlap matrix  $S^i$  for the orbitals in  $T^i$ . Orthogonalize  $T^i$  with symmetric orthogonalization [i.e., using  $(S^i)^{-1/2}$ ].
- (d) End if we have completed the last importance class.
- (e) Loop over atoms  $a$ .
  - (i) Project out the orbitals  $Y_a^i$  from the set of orbitals  $Y_a$ . We have now redefined  $Y_a$ .
- (f) Set  $i=i+1$ .

### III. RESULTS

#### A. Computational analysis of orbitals

The algorithm presented above was implemented and interfaced with the Q-CHEM quantum chemistry package.<sup>40</sup> In order to demonstrate the inapplicability of Boys localization for the virtual space, we first compute the number of Jacobi sweeps necessary to get the localization to converge for alkanes of various lengths and with different basis sets. We defined convergence as  $\max_{ij} |R_{ij} - R_{ji}| < 10^{-6}$  or whenever all terms in the computation are less than  $10^{-14}$  (i.e., close to  $\epsilon$ ). Here  $(R_{ij} - R_{ji})$  is the derivative of the Boys functional,

$$R_{ij} = \langle i | \mathbf{r} | i \rangle \cdot \langle i | \mathbf{r} | j \rangle. \quad (19)$$

For pentane ( $C_5H_{12}$ ), in an all-*trans* geometry in a 6-31G\* basis, 109 Jacobi sweeps are required for the convergence of localization of the virtual space; for decane ( $C_{10}H_{22}$ ), 218 Jacobi sweeps are required. (In both cases, the valence virtual space converges in under 15 iterations.) One immediately concludes that the Boys localization procedure is very inefficient for the full virtual space, as it requires hundreds of iterative sweeps (each of which scale as  $N^3$ ) to converge even for simple alkanes in a 6-31G\* basis. Furthermore, for the full virtual space of ( $C_{20}H_{42}$ ) in a helical geometry, one finds that the convergence of the Boys localization function requires 524 Jacobi sweeps for a 6-31G(*d*) basis and 2026 steps for the 6-31G(*2df*) basis. (Again, in both cases, the valence virtual space converges in under 15 steps.) Hence, the clear implication is that Boys localization becomes much harder as the dimensionality and complexity of the whole virtual space grow. In fact, we have found empirically that Boys localization of the full virtual space is simply prohibitive for large systems. From a positive perspective, however, it is clear that the valence virtuals can be well localized with a Boys functional, as we had hoped.

In contrast with the Boys procedure, our algorithm is fast and behaves quite well when dealing with large alkanes. In Fig. 1, we plot the orbital spread  $(\langle r^2 \rangle - \langle r \rangle^2)^{1/2}$  for all-*trans* alkanes  $C_{10}H_{22}$ ,  $C_{20}H_{42}$ , and  $C_{40}H_{82}$  in a 6-31G\* basis. One can see that our orbitals appear qualitatively similar as the size of the alkane grows.

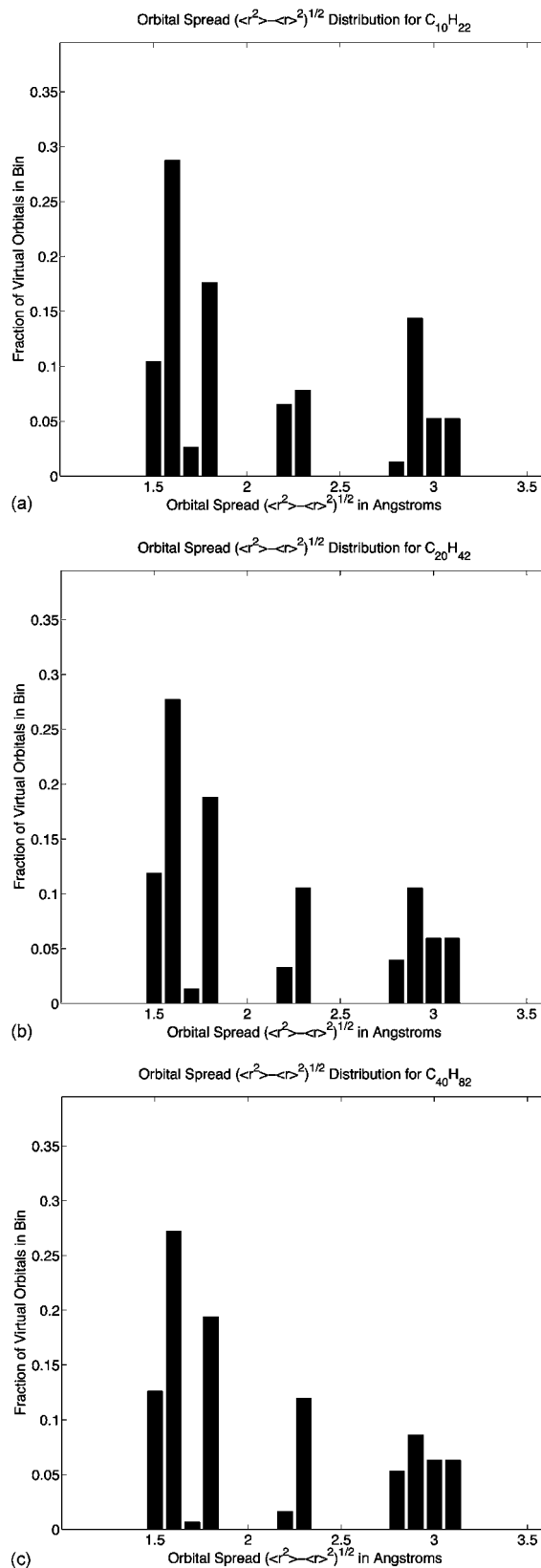


FIG. 1. (a) The distribution of orbital spread for all-*trans*  $C_{10}H_{22}$  in a 6-31G\* basis. Orbitals were computed via our algorithm, using one importance class only. (b) The distribution of orbital spread for all-*trans*  $C_{20}H_{42}$  in a 6-31G\* basis. Orbitals were computed via our algorithm, using one importance class only. (c) The distribution of orbital spread for all-*trans*  $C_{40}H_{82}$  in a 6-31G\* basis. Orbitals were computed via our algorithm, using one importance class only.

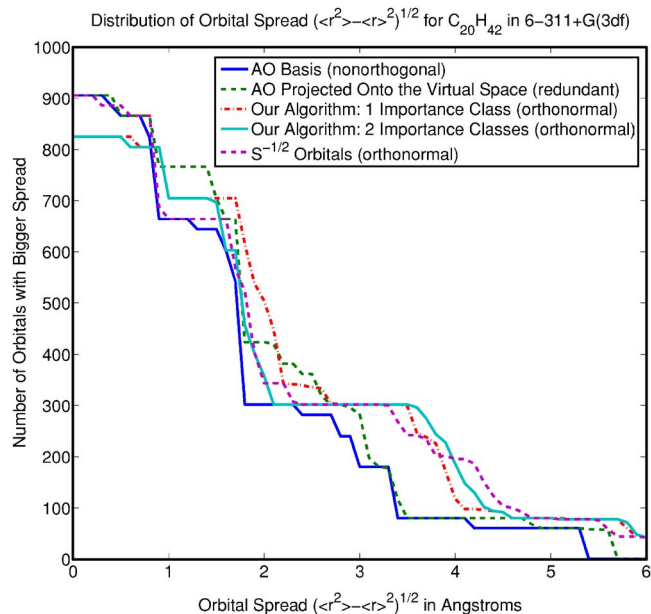


FIG. 2. The distribution of orbital spread for  $C_{20}H_{42}$  in a helical conformation in a 6-311+G(3df) basis. Here we plot the distribution for the AO basis, the AO basis projected into the virtual space, the  $S^{-1/2}$  orbitals, and the orbitals from our algorithm with either one or two importance classes. Above  $x=x_0$  we show the number of orbitals with spread bigger than  $x_0$ . Our orbitals are not redundant and only cover the virtual space; hence they have a different limit at  $x=0$ . Note that two importance classes tighten the smaller functions but slightly loosen the more diffuse.

In Fig. 2, we show the spreads of our orbitals relative to the AO basis, the AO space projected onto the virtual space, and the  $S^{-1/2}$  orthonormal orbitals. The system is the alkane  $C_{20}H_{42}$  in a helical conformation in the 6-311+G(3df) basis set. This plot is a histogram integrated from the right. Above  $x_0$  on the  $x$  axis, we show the number of orbitals with a spread greater than  $x_0$ . Our algorithm produces only as many functions as the dimension of the virtual space, while the AO basis, projected AO's, and  $S^{-1/2}$  orbitals obviously have the same size as the dimensionality of the full AO space. For this reason, all five curves do not agree at the point  $x=0$ .

From the data, we conclude that our procedure does produce local virtual functions, particularly maintaining the locality of the tightest virtual functions. For diffuse functions, our orbitals are clearly much larger than both the AO's and the projected AO's. In fact, our diffuse orbitals expand much in the same way that the  $S^{-1/2}$  orbitals expand. Figure 2 shows clearly both how one can make tight localized orthonormal virtual orbitals and simultaneously the price that one pays for orthonormalization by producing diffuse functions which are extra-expanded. This is precisely the trade-off we consider when deciding how many importance classes to choose from. If one requires the largest number of the smallest functions possible then, as the data show, two importance classes are better than one. (We find three importance classes to be unnecessary, though.) For the smallest functions, orthonormal orbitals can be tighter than the projected AO's.

In our next graph, Fig. 3, we demonstrate the change in our virtual orbitals when a set of diffuse functions is added. Again, we make an integrated histogram of the orbital spread for the alkane  $C_{20}H_{42}$  in a helical conformation with a

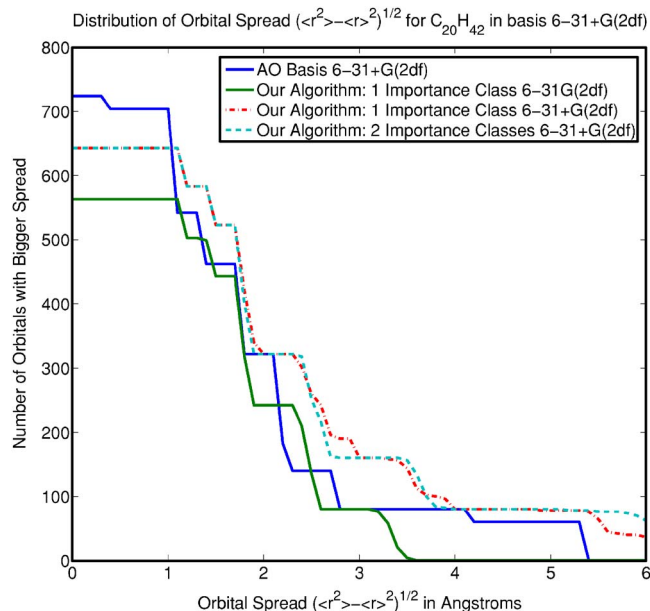


FIG. 3. The distribution of orbital spread for  $C_{20}H_{42}$  in a helical conformation in a 6-31+G(2df) basis. Here we plot the distribution for the AO basis, and the orbitals from our algorithm with either one or two importance classes. We also show the orbitals from our algorithm in a 6-31G(2df) basis. Note that when a diffuse set of equations is added, we must use two importance classes if we want to best preserve the locality of the tight functions. (a) One  $d$  hard virtual for  $C_2H_6$ , (b) one  $d$  hard virtual for  $C_2H_4$ , (c) one  $d$  hard virtual for  $C_2H_2$ , and (d) one  $d$  hard virtual for  $C_6H_6$ .

6-31G(2df) basis. The point of this diagram is to show that, when the diffuse functions are added to make 6-31+G(2df), the set of hard virtuals loses some locality if only one importance class is used. However, when two importance classes are employed, one for the tight functions and the other for the diffuse functions, our first orbitals change only negligibly.

## B. Qualitative analysis of orbitals

In Fig. 4, we compare one  $d$  hard-virtual orbital on a carbon atom across a range of systems:  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ , and  $C_6H_6$  (benzene). The reader must remark how similar this hard virtual looks across four very different molecules with different hybridizations, coordination numbers, and aromaticity. This remarkable similarity is indeed a pictorial confirmation of our initial hypothesis that one can reliably partition the AO vector space into a minimal basis and atom-centered hard virtuals that resemble proto-HV's (which are independent of the geometry of the molecule).

## IV. DISCUSSION

The algorithm described in this paper provides a stable method for computing well-defined, localized orthonormal virtual orbitals depending smoothly on nuclear coordinates.<sup>41</sup> The algorithm is fast with the rate-determining step being the  $N^3$  diagonalization of the overlap matrix in the last step. This will usually be of less effort than one SCF iteration. Additionally, it requires minimal quadratic storage.

The strength of our algorithm is based fundamentally on the locality of the AO basis, the propensity of the free atomic

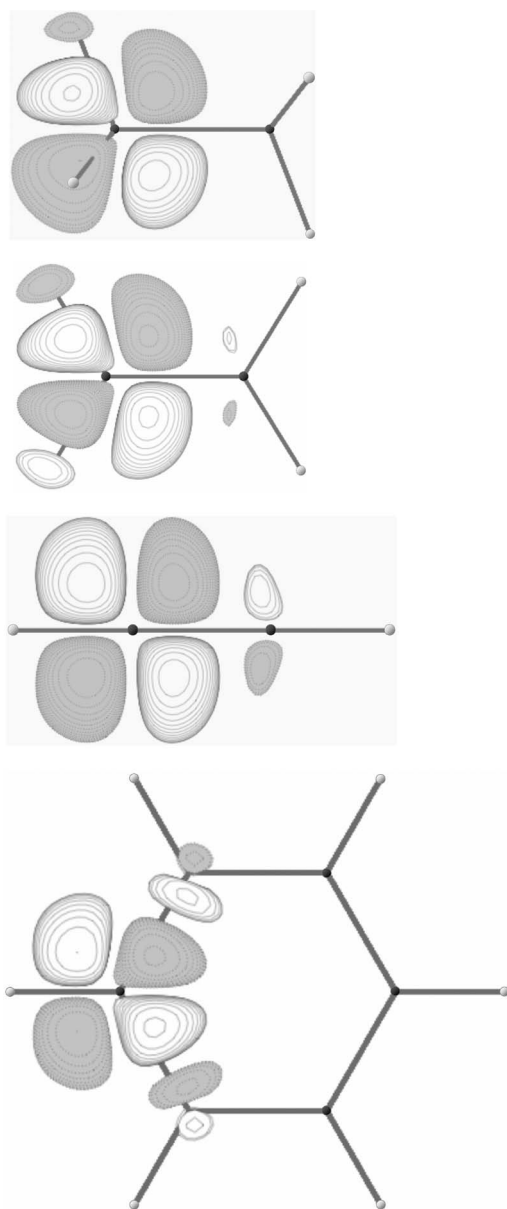


FIG. 4. One  $d$  hard virtual for a carbon atom plotted across  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ , and  $C_6H_6$ . The basis is 6-31+G<sup>\*\*</sup>. The orbitals were constructed with our algorithm, using two importance classes.

orbitals (represented by the STO-3G basis) to capture most of the occupied space, and the existence of atom-centered hard virtuals. Our algorithm is able to produce well-defined, smoothly varying hard-virtual orbitals precisely because it does not optimize any localization function, which would necessarily grow more difficult and unstable as the basis size grows. Our algorithm does rely on the localization of the valence virtual space by the optimization of a defining function (e.g., Boys), but we expect this to be unproblematic: valence virtual orbitals, such as occupied orbitals, are physically meaningful and hence should correspond to well-defined, stable isolated minima in the space of rotations.

According to the data presented in Sec. V, the virtual orbitals constructed from our algorithm keep the same character for alkanes of growing size. From this we conclude that our algorithm scales correctly for growing virtual spaces of

the same character. This is reassuring; so is the pictorial result that hard-virtual orbitals look alike for carbon atoms in different molecules. Furthermore and most surprisingly, our orbitals appear almost as small as the AO's projected onto the virtual space. When there are tight and diffuse functions in the AO basis, the key step in our procedure which accounts for the locality of our orbitals is the retightening of the hard orbitals on every atom to the proto-HV's. Using this retightening step, we may later separate our orbitals into two importance classes. We find that our tight orbitals have the same or better size distribution as the projected AO's for tight functions; for diffuse functions, our orbitals clearly expand to accommodate orthonormality. In fact, we note that our orbitals are consistently as local as the  $S^{-1/2}$  orbitals that orthonormalize the full AO space. This implies that we are attaining highly satisfactory localization of the much more complex virtual space. Our algorithm is still not comparable in sparsity to the Cholesky decomposition of the AO basis, but the sparsity of the  $S^{-1/2}$  orbitals is also acceptable. We note that the Cholesky factorization does not produce globally smooth or even continuous orbitals, as it relies on the ordering of atomic orbitals; by contrast, the  $S^{-1/2}$  algorithm always produces continuous orbitals that vary smoothly with atomic position.

Several caveats should now be made about the stability of the algorithm presented above. First, the algorithm presented here will fail when the occupied space of a given molecule in a given geometry cannot be well represented in a STO-3G basis. Though this is not common for molecules made up of first row elements, it will certainly be true for hypervalent compounds (such as  $SF_6$ ) made up of heavier elements. Transition metal compounds would also likely have an occupied space not well represented by STO-3G. For such cases, an obvious fix would be to change the definition of the minimal basis space and the hard-virtual space. For example, one could use the STO-3G\* basis, instead of STO-3G, to create a bigger and more physical minimal basis space and a smaller hard-virtual space (with different proto-HV's).

Second and more difficult, the algorithm designed here relies on the separation between the two eigenvalues  $\lambda_{N_M}$  and  $\lambda_{N_{M+1}}$  of the overlap matrix of the projected atomic orbitals. Intuitively, we believe that this should always be the case, as this separation tells us how the minimal basis has a strong component of full dimension in the AO space for every atom. So far, we have always seen a separation. Without diffuse functions, we in general find  $\lambda_{N_{M+1}}/\lambda_{N_M} > 5$ . This factor can be as low as 2 when there are diffuse functions around. Of course, we cannot guarantee that we will always have such a separation. In the case that  $\lambda_{N_M} \approx \lambda_{N_{M+1}}$ , we would have a two-dimensional subspace of infinitely many equivalent choices for which eigenvectors to keep and which to throw away. This ambiguity would mean that our localized virtual orbitals would no longer depend smoothly on nuclear position. We mention here, however, that when such a case arises, our whole procedure will likely fail. Such a situation would mean that our proto-HV's do not well resemble the atomic virtual space, and our retightening procedure would



fail [i.e., we cannot compute the  $-1/2$  power in Eq. (16)]. We have not yet seen such a case to date; we have always had  $\lambda_{N_{M+1}}/\lambda_{N_M} > 2$ .

Third, even if we do have a large gap in eigenvalues  $\lambda_{N_M} \ll \lambda_{N_{M+1}}$  and we are able to compute localized, orthonormal hard-virtual functions on each atom, we are never guaranteed that, at the very end of our algorithm, we will have enough linear independence in order to stably orthogonalize the collections of hard-virtual orbitals on different atoms. In other words, when we compute the overlap  $\mathbf{S}$  matrix between virtual functions on different atoms in the end, we do not know what will be the condition number of the  $\mathbf{S}$  matrix. If the hard-virtual space is well decomposed into different atomic blocks, then the  $\mathbf{S}$  matrix should have a small condition number and the algorithm should be stable. If not, the algorithm could conceivably give spurious results. Again, this has not yet been a problem.

This does, however, lead to our fourth and final point. The reader should note that as one considers larger and larger AO bases for a given geometry, say, from 6-31G\* to 6-311++G\*\*, the AO basis itself can easily become linearly dependent. Or more precisely, the condition number of the overlap matrix of the AO basis becomes enormous, and the basis is “effectively” linearly dependent. In this case, one clearly cannot apply our algorithm as above, where we seek a fixed number of orthonormal hard-virtual atomic orbitals. In fact, the problem stated in the previous paragraph must occur, because we simply cannot form a stable orthonormal basis for a virtual space with smaller dimension than the number of vectors that we have. From a philosophical level, the AO basis no longer has truly independent functions on individual atoms and is not atom centered. So our scheme, which uses the AO basis as the crucial ingredient towards atom-centered orthonormal virtuals, is bound to fail. In the Appendix, we discuss what we can do in this case. One certainly cannot find smoothly varying, localized, orthonormal virtual functions but at least one can compute well-defined, localized, orthonormal virtual functions.

Notwithstanding these caveats, in the future, the orbitals produced by this algorithm should be quite applicable to local-correlation calculations for several reasons. First, they are produced by a stable and quite fast algorithm. Second, they are almost as sparse as projecting the AO's on the virtual space with the added bonus of being orthonormal—orthonormality greatly simplifies local-correlation calculations. Third, our orbitals are smoothly dependent on atomic position, so they may be used to construct potential-energy curves. For all of these reasons, our algorithm and its corresponding localized virtual orbitals may potentially replace projected AO's as a basis for the virtual space in future local-correlation calculations.

## V. CONCLUSIONS

The localization of the virtual space is a difficult computational problem because the virtual space in quantum chemistry has little to do with chemistry and much more in common with the huge, infinitely dimensional function space of all normalized orbitals. Given the enormity and complex-

ity of this function space, we believe that any algorithm which localizes virtual orbitals by the optimization of a localization function cannot give well-defined (much less smoothly varying) orbitals in a timely manner. For this reason, we have designed an algorithm which relies only on the locality of our AO basis and our assumption that electrons stay predominantly in a minimal basis space. The success of our algorithm to date demonstrates that our assumption is not unreasonable, and that, despite the complexity of the virtual space, one can find localized orthonormal virtual orbitals for molecules in a local AO basis. This conclusion should now allow computational chemists to construct new local-correlation algorithms using only orthonormal (occupied and virtual) orbitals and without need for redundant basis sets.

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## APPENDIX: AO LINEAR DEPENDENCE

When one works on a system (perhaps an anion) with a huge basis set, one sometimes encounters linear dependence of the AO basis for the calculation. In this case, as mentioned above, our method is inapplicable. For example, in the basis set 6-31+G, the overlap matrix  $\mathbf{S}$  of the AO basis for  $\text{C}_{20}\text{H}_{42}$  has as its smallest value  $\lambda_0 \approx 10^{-7}$  and a condition number of  $10^8$ . If our threshold for linear dependence is  $10^{-6}$ , then there are two linear dependencies—i.e., there are two eigenvalues less than  $10^{-6}$ .

For such a case, smooth localized orthonormal orbitals are clearly an impossibility. They must not exist because the effective size of the vector space changes discontinuously as calculated by a computer (even though the smallest eigenvalue of  $\mathbf{S}$  changes continuously). We will be satisfied if we can produce the correct number of well-defined localized orthonormal orbitals. With that in mind, we propose the following procedure:

- (1) Let  $N$  be the number of AO basis functions. Let  $W$  be the set of AO's. Let  $c_0$  be the threshold for linear dependence.
- (2) Loop from  $i=1, \dots, N$ .
  - (a) Form the overlap  $\mathbf{S}$  matrix for all functions in  $W$  and diagonalize.
  - (b) Let  $\lambda_0$  be the smallest eigenvalue of  $\mathbf{S}(W)$ . If  $\lambda_0 > c_0$ , break out of the loop; we are done.
  - (c) Let  $v_0$  be the vector corresponding to  $\lambda_0$ . If the eigenvalue  $\lambda_0$  is degenerate, sort this list in some standard way (i.e., by dipole matrix elements, quadrupole matrix elements, etc.). Pick  $v_0$  as the first vector on this list.



- (d) Project  $v_0$  onto every vector in  $W$ . Let  $\phi_0$  be the vector in  $W$  with the largest projection. Again, if several vectors in  $W$  have the same size projection, order the list in terms of dipole and quadrupole moments and choose one uniquely.
- (e) Remove the atomic orbital  $\phi_0$  from  $W$ .
- (3)  $W$  is now a well-defined subset of the full set of AO's and there are exactly  $N-i$  linearly independent AO vectors in  $W$ . Once we replace the full set of AO's by the set  $W$ , we can calculate the hard-virtual set in the standard way described above.

With this trick, our algorithm will find well-defined, orthonormal, localized orbitals spanning the effective virtual space. For example, in the case of  $C_{20}H_{42}$  in a linear conformation in the 6-31+G basis (with a threshold of  $10^{-6}$ ), two degeneracies arise. If we label our carbon atoms  $C_1, \dots, C_{20}$ , our procedure eliminates the diffuse  $s$  functions on  $C_{10}$  and  $C_{13}$ . We then find that the remaining set of  $N-2$  AO's is linearly independent, and we may proceed to calculate the orthonormal hard-virtual orbitals in the usual way.

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