Quasiparticle virtual orbitals in electron propagator calculations

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The computational limits of accurate electron propagator methods for the calculation of electron binding energies of large molecules are usually determined by the rank of the virtual orbital space. Electron density difference matrices that correspond to these transition energies in the second-order quasiparticle approximation may be used to obtain a virtual orbital space of reduced rank that introduces only minor deviations with respect to the results produced with the full, original set of virtual orbitals. Numerical tests show the superior accuracy and efficiency of this approach compared to the usual practice of omission of virtual orbitals with the highest energies. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2902288]

I. INTRODUCTION

Electron propagator theory[1–5] is the foundation of powerful computational procedures for describing a variety of electron detachment and attachment processes. Approximations that are designed for the determination of the valence electron binding energies of closed-shell molecules, such as the partial third order[6,7] (P3) and outer valence Green's function[2,8] (OVGF) methods, have been successfully applied to many experimental problems, ranging from diatomic molecules to nucleotides[9,10] and substituted porphyrins.[11,12] Interpretations of experiments on even larger molecules and ions may be based on *ab initio* electron propagator calculations which are capable of predicting vertical transition energies within approximately 0.25 eV of the experiment.

Limits to the application of the P3 and OVGF methods to larger systems are established by the number of arithmetic operations and the size of disk memory that such calculations require. In P3 calculations of electron detachment energies, the arithmetic bottleneck is encountered in the partial transformation that yields electron repulsion integrals in the Hartree–Fock basis with up to three virtual orbital indices. Another bottleneck is encountered in the evaluation of self-energy matrix elements, where the limiting operation scales arithmetically with the third power of the number of virtual orbitals. In OVGF calculations, the arithmetic bottleneck occurs in an operation with a fourth-power dependence on the dimension of the virtual orbital space.[13] In both cases, the largest intermediates that must be stored have three virtual orbital indices.

A systematic procedure for the reduction of the virtual orbital space that minimizes deviations from ordinary calculations is therefore needed. In calculations that probe the limits of computational resources, canonical virtual orbitals with the highest energies often have been omitted from integral transformations and subsequent evaluations of self-energy matrix elements. In practice, the stability of the results with respect to the energetic cutoff must be verified by a series of calculations.

An alternative criterion for the reduction of the virtual orbital space is provided by effective electron-density difference matrices that correspond to electron binding energies.[14,15] Such matrices are needed to evaluate the nuclear gradients of the latter transition energies and also may be used to determine differences in one-electron properties between states with N and $N \pm 1$ electrons. Explicit expressions for the elements of these matrices were derived for the relatively simple second-order self-energy approximation.

Here, the method described has three steps. First, second-order, quasiparticle (diagonal self-energy matrix) electron propagator calculations are performed. In the second stage, the virtual orbital space's rank is reduced using the electron density difference matrix that corresponds to the second-order, quasiparticle calculation. Finally, more advanced electron propagator methods such as P3 or OVGF are executed with the new virtual orbitals. The latter are designated quasiparticle virtual orbitals or QVOs. Thus, accurate determinations of relaxation and correlation corrections to Koopmans results are obtained with a reduced virtual orbital space that is adapted to the electron attachment or detachment process under consideration.

The paper is organized as follows. In Sec. II, the QVOs method is described. A performance analysis is presented in Sec. III. Illustrative applications to benzene and borazine are presented in Sec. IV. Conclusions are given in Sec. V.

II. METHOD

In the diagonal, second-order approximation to the self-energy of the electron propagator, the Dyson equation reads as

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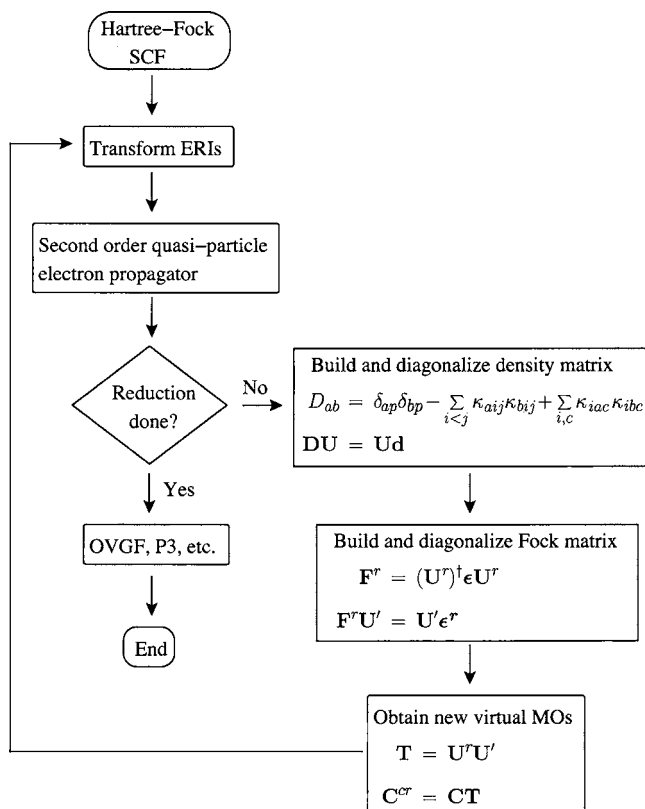
FIG. 1. Flowchart of the algorithm used for the reduction of the virtual space.

FIG. 2. Approximation error as function of percentage of orbitals eliminated.

$$\omega_p = \epsilon_p + \Sigma_{pp}(\omega_p), \tag{1}$$

where ϵ_p is the pth canonical orbital energy. Relaxation and correlation corrections to the Koopmans result (ϵ_p) reside in the energy-dependent self-energy, where

$$\Sigma_{pp}(\omega_p) = \frac{1}{2} \sum_{iab} \frac{|\langle pi \| ab \rangle|^2}{\omega_p + \epsilon_i - \epsilon_a - \epsilon_b} + \frac{1}{2} \sum_{aij} \frac{|\langle pa \| ij \rangle|^2}{\omega_p + \epsilon_a - \epsilon_i - \epsilon_j}, \tag{2}$$

where $p, q, r, \ldots$, label general spin orbitals, $i, j, k, \ldots$, label occupied spin orbitals, and $a, b, c, \ldots$, label virtual spin orbitals. Self-consistent (pole) energies ω_p satisfy Eq. (1).

Elements of the first-order, density-difference matrix in the virtual-virtual block are given by[14,15]

TABLE I. First ionization energy (eV) of H_2O vs rank of virtual orbital space.

%	N_{vir}	EP2	EP3	OVGF	P3
100	110	11.663	13.332	12.809	12.765
90	99	11.663	13.329	12.806	12.765
80	88	11.662	13.324	12.800	12.764
70	77	11.660	13.318	12.795	12.761
60	66	11.655	13.310	12.788	12.756
50	55	11.642	13.308	12.787	12.741
40	44	11.614	13.292	12.775	12.708
30	33	11.553	13.246	12.735	12.638

$$D_{ab} = \delta_{ap}\delta_{bp} - \sum_{i<j} \kappa_{aij}\kappa_{bij} + \sum_{i,c} \kappa_{iac}\kappa_{ibc} \tag{3}$$

such that

$$\kappa_{qst} \equiv \frac{\langle pq \| st \rangle}{\omega_p + \epsilon_q - \epsilon_s - \epsilon_t}, \tag{4}$$

where ω_p is the second-order pole energy associated with the pth spin orbital. For the case of electron *detachment* energies, the first term on the right hand side of Eq. (3) vanishes, for p is an occupied spin orbital. The matrix $\mathbf{D}$ may be block diagonalized when spatial symmetry is exploited in the calculation.

In actual computer implementations, the molecular orbitals (MOs) are expressed as linear combinations of atomic orbitals,

$$\varphi_a(\mathbf{r}) = \sum_{\mu} C_{\mu a}\mu(\mathbf{r}). \tag{5}$$

Here, $\varphi_a(\mathbf{r})$ is a virtual MO and $\mu(\mathbf{r})$ represents an atomic basis function. The diagonalization of $\mathbf{D}$ yields a new set of noncanonical, virtual MOs that is related to the original one by a unitary transformation,

$$\mathbf{C}^d = \mathbf{CU}, \tag{6}$$

where $\mathbf{C}^d$ describes the new set of virtual MOs, the transformation matrix $\mathbf{U}$ satisfies

$$\mathbf{DU} = \mathbf{Ud} \tag{7}$$

and $\mathbf{d}$ is a diagonal matrix containing the eigenvalues of $\mathbf{D}$. Positive and negative eigenvalues are found, for the $\mathbf{D}$ matrix describes an electronic density difference. In the method proposed here, eigenvectors (columns of $\mathbf{U}$) corresponding to eigenvalues with the smallest absolute values are discarded. In this way, the virtual space is reduced. In general, the discarded columns are in the middle of the eigenvalue-ordered eigenvectors of $\mathbf{U}$,

$$\mathbf{U} = (\mathbf{U}^{active1}|\mathbf{U}^{discarded}|\mathbf{U}^{active2}). \tag{8}$$

The active space is built by forming a new reduction matrix as follows:

$$\mathbf{U}^r = (\mathbf{U}^{active1}|\mathbf{U}^{active2}). \tag{9}$$

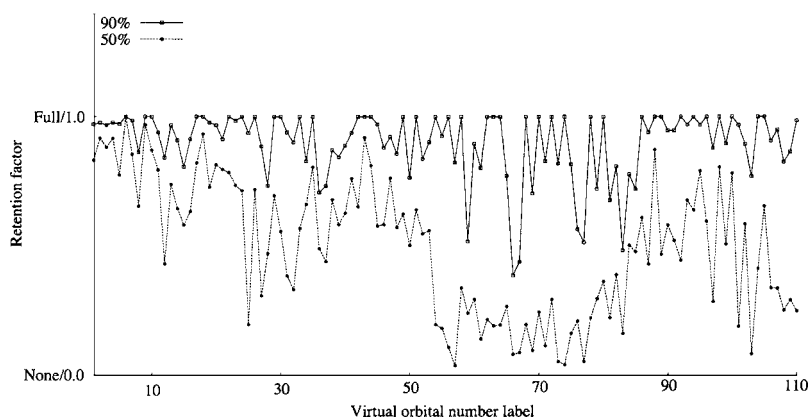Therefore, noncanonical MOs of the reduced virtual space are given by

FIG. 3. Retention coefficients for the H_2O molecule with the cc-pVQZ basis set.

$$\mathbf{C}^r = \mathbf{C}\mathbf{U}^r. \qquad (10)$$

Because the spectral range of the **D** matrix considerably varies with the system type and size, the use of eigenvalue thresholds is not recommended. Instead, we have eliminated certain percentages of the virtual orbitals.

In general, these new, virtual orbitals are not eigenfunctions of the Fock operator. In order to obtain orbital energies that are consistent with the transformed active orbitals, the virtual-virtual block of the Fock matrix expressed in this reduced orbital space must be diagonalized. This step results in a second transformation but only for the active space,

$$\mathbf{C}^{cr} = \mathbf{C}^r\mathbf{U}' = \mathbf{C}\mathbf{U}^r\mathbf{U}' = \mathbf{C}\mathbf{T}, \qquad (11)$$

where **T** is the full transformation matrix required to build the reduced, canonical, virtual space from the original canonical orbitals, and where the matrix $\mathbf{U}'$ contains the eigenvectors of the Fock matrix in the reduced virtual space such that

$$\mathbf{F}^r\mathbf{U}' = \mathbf{U}'\boldsymbol{\epsilon}^r \qquad (12)$$

and

$$\mathbf{F}^r = (\mathbf{U}^r)^\dagger \boldsymbol{\epsilon}\mathbf{U}^r. \qquad (13)$$

Note that $\boldsymbol{\epsilon}$ and $\boldsymbol{\epsilon}^r$ are diagonal matrices with ranks corresponding to the original and the reduced virtual spaces, respectively.

A flow chart of the algorithm is shown in Fig. 1. To calculate the effective density-difference matrix with Eq. (3), the poles of the propagator in the second-order, diagonal self-energy approximation are needed. Such calculations are very efficient;[16] their arithmetic scaling is just cubic. The virtual orbital space is reduced subsequently as described above. Finally, higher-order calculations are done with the reduced virtual space. After the second (or subsequent) transformation of electron repulsion integrals, the second-order, quasiparticle approximation is executed with the reduced virtual space. Thus, the error found in the second-order calculation with respect to the result obtained with the full virtual space can be used as a preliminary estimate of the quality of the reduced virtual space.

III. PERFORMANCE

This section reports some tests of the procedure discussed above. All calculations were performed with the

GAUSSIAN 03 suite of programs[17] and a modified version of its electron propagator link. The advantages of this approach compared to the omission of unmodified virtual orbitals according to their energies are discussed below.

A. Accuracy and stability

A threshold for the absolute value of an element of the diagonal **d** matrix could serve as a criterion for the formation of a reduced virtual space. However, the optimum value depends on the nature of the system, the electron binding energy to be treated, and the quality of the atomic basis set. Therefore, it is more practical to demand the elimination of a given percentage of the virtual orbitals. Table I shows second-order, third-order, P3 and OVGF results when this technique is applied to the water molecule using the cc-pVQZ basis set.[18] Approximately 60% of the virtual orbital space's rank can be eliminated while keeping the approximation error smaller than approximately 0.05 eV.

One may compare the present technique with simple omission of the original virtual orbitals with the highest energies. Direct elimination of a few, unmodified virtual orbitals results in very large errors. Figure 2 shows errors versus the number of orbitals removed in the P3 calculations. The reduction via the QVO procedure not only results in smaller errors for a virtual orbital space of a given rank but also in a much more stable series of approximations. The QVO procedure has the minor disadvantage of requiring different virtual spaces for each transition energy, whereas direct elimination of unmodified virtual orbitals may be applied to many transition energies. However, determination of QVOs is not a
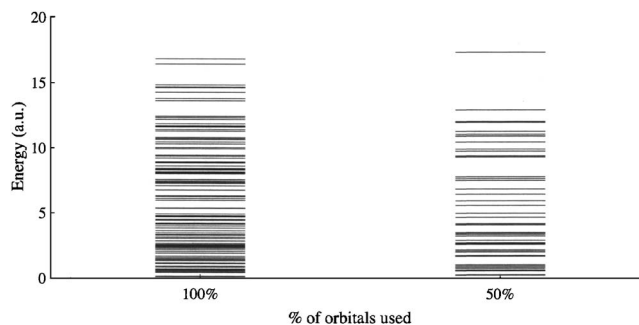

FIG. 4. Change in orbital energies (value about 44 not plotted for the 100% case).
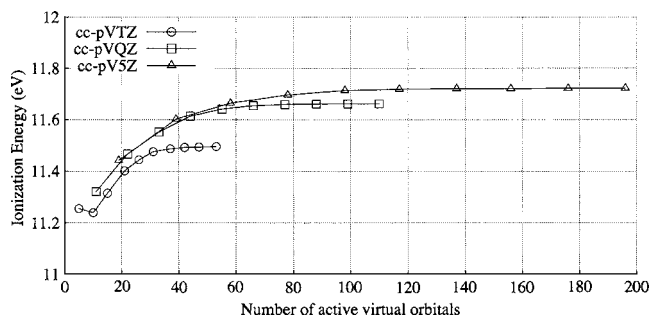
FIG. 5. Error introduced in second-order electron propagator calculations by reduction of virtual space using the QVO procedure.

FIG. 7. Error introduced in OVGF electron propagator calculations by reduction of virtual space using the QVO procedure.

rate-limiting step and requires a smaller virtual space for a given level of accuracy. In practice, it is likely to achieve higher accuracy with less effort.

B. Characterization of the reduced virtual space

The full transformation between the initial and the reduced virtual spaces is contained in the rectangular **T** matrix. Therefore, for an initial, virtual orbital, $\mathbf{c}_a$, the projection onto the reduced space is given by

$$\mathbf{P}_a = \mathbf{C}'(\mathbf{C}')^\dagger \mathbf{S}\mathbf{c}_a = \mathbf{C}\mathbf{T}(\mathbf{C}\mathbf{T})^\dagger \mathbf{S}\mathbf{c}_a = \mathbf{C}\mathbf{T}\mathbf{T}^\dagger \mathbf{C}^\dagger \mathbf{S}\mathbf{c}_a, \quad (14)$$

where **S** is the atomic orbital overlap matrix. Because of the orthogonality of the original virtual orbitals, $\mathbf{C}^\dagger \mathbf{S}\mathbf{c}_a$ yields a column vector with all entries equal to zero except the ath row, which contains a value of unity. A retention coefficient may be defined as the overlap between the original virtual orbital a and its projection onto the new reduced virtual space,

$$r_a \equiv \mathbf{c}_a^\dagger \mathbf{S}\mathbf{P}_a = \sum_b |T_{ab}|^2. \quad (15)$$

By construction, $0 \leq r_a \leq 1$ for all a. A value of zero corresponds to the full removal of the orbital a from the calculation, whereas a value of unity results when the orbital is completely retained in the reduced virtual space. However, the identity of the orbital will be lost in most cases and its contributions will be distributed over many of the new canonical orbitals.

The retention coefficient r_a is useful for monitoring the selection process and to gain understanding of the systems under study. For example, if one wishes to keep a certain initial virtual orbital, removal of transformed orbitals that
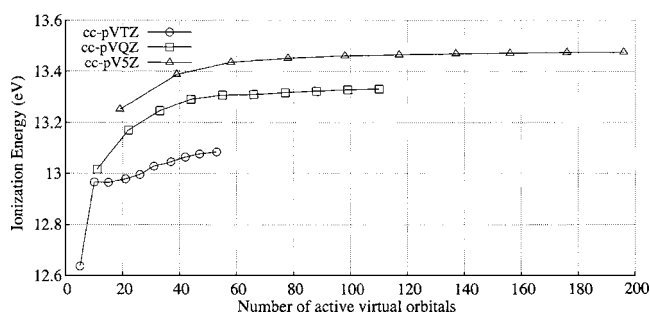
have a non-negligible overlap with it should be avoided. This idea is very simple to implement in the selection process and may be combined with other selection methods.

Figure 3 shows the retention coefficients for all 110 unmodified virtual orbitals when the rank of the virtual space is reduced to 90% or 50% of its original size. Even when the rank of the virtual space is reduced only by 11, the coefficients of many orbitals are affected. On the other hand, a 50% reduction of the virtual space does not necessarily imply the total removal of any of the original canonical orbitals. Figure 3 also demonstrates that virtual orbitals with the highest energies are not necessarily less relevant for the evaluation of a given ionization energy.

Figure 4 shows the change in the eigenvalue spectrum of the Fock matrix due to the virtual space reduction. (A single energy in the original virtual space lies outside the range of the plotted ordinate.) Certain energy ranges become markedly depleted of orbitals after performing the QVO procedure.

C. Rank reduction and basis sets

The H_2O molecule was treated with four correlation-consistent basis sets: cc-pVXZ, with X=T, Q, 5.[18] The results of second-order, third-order, OVGF, and P3 quasiparticle electron propagator calculations obtained with varying percentages of the rank of the virtual orbital space are shown in Figs. 5–8, respectively. As the correlation-consistent basis grows, it is possible to eliminate higher percentages of virtual orbitals while introducing only small errors with respect to the calculation with the original virtual space. However, when comparing basis sets, a smaller percentage for the reduced virtual space does not imply a smaller number of vir-

FIG. 6. Error introduced in third-order electron propagator calculations by reduction of virtual space using the QVO procedure.

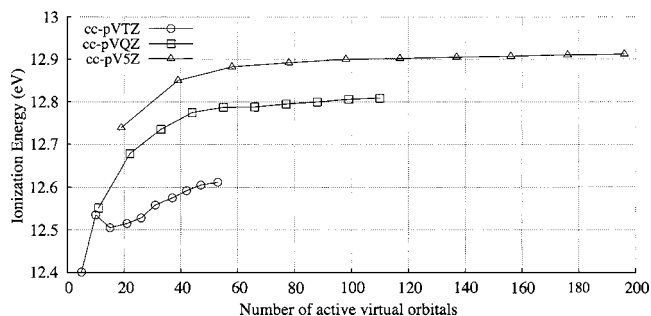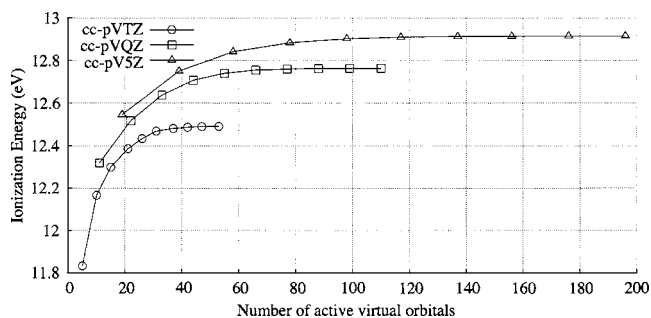FIG. 8. Error introduced in P3 electron propagator calculations by reduction of virtual space using the QVO procedure.

TABLE II. cc-pVTZ ionization energies (eV) with 50% virtual orbital space reduction.

Molecule	Orbital	EP2	EP3	OVGF	P3	Expt.[a]
HF	1π	14.60	16.75	15.97	15.83	16.19
	3σ	18.84	20.40	19.79	19.71	20.00
N_2	$1\pi_u$	16.90	16.35	16.52	17.03	16.98
	$3\sigma_g$	14.85	15.78	15.36	15.75	15.60
	$2\sigma_u$	18.06	19.74	18.98	19.13	18.78
CO	5σ	13.99	13.85	13.76	14.15	14.01
	1π	16.26	17.26	16.98	16.90	16.91
	4σ	18.32	21.48	20.11	20.01	19.72
F_2	$1\pi_g$	14.02	16.33	15.46	15.38	15.83
	$3\sigma_g$	20.28	21.05	20.91	20.78	21.1
	$1\pi_u$	17.26	19.91	18.90	18.71	18.8
H_2O	$1b_1$	11.44	13.00	12.53	12.43	12.78
	$3a_1$	13.79	15.21	14.80	14.68	14.74
	$1b_2$	18.00	19.00	18.54	18.62	18.51
C_2H_4	$1b_{3u}$	10.30	10.45	10.42	10.52	10.51
	$1b_{3g}$	12.61	13.02	12.91	12.82	12.85
	$3a_g$	14.40	14.83	14.62	14.80	14.66
	$1b_{2u}$	15.80	16.27	16.07	16.00	15.87
	$2b_{1u}$	19.26	19.71	19.54	19.36	19.23
Av.$|\Delta_{expt.}|$		0.74	0.48	0.20	0.18	
Av.$|\Delta_{100}|$		0.11	0.13	0.10	0.13	

[a]See Ref. 6.

tual orbitals. For example, two P3 calculations, one with a smaller atomic basis and a relatively high fraction of virtual orbitals and another with a larger atomic basis and a relatively small fraction of virtual orbitals, could have virtual orbital spaces with the same rank. Should the latter calculation produce more accurate results because of the quality of the atomic basis set and the insignificance of the errors introduced by the virtual space reduction, its chief remaining disadvantages would arise from a more difficult Hartree–Fock step and a more demanding initial, second-order quasiparticle calculation. Neither of the latter steps would constitute a computational bottleneck. The absence of curve crossings in Figs. 6–8 suggests that this reasoning is likely to be applicable in many calculations. Therefore, employment of more flexible atomic basis sets may be facilitated by the QVO procedure.

D. Molecular test set

Table II lists the results obtained with the cc-pVTZ basis set for various, closed-shell molecules when the rank of the virtual space is reduced by 50%. The bottom line shows that an average absolute deviation of about 0.1 eV with respect to calculations with unmodified virtual orbitals (see Ref. 6) is introduced by the QVO procedure for all four types of quasiparticle calculations. A deviation of about 0.1 eV also was obtained when using the cc-pVQZ basis set. Such errors are smaller than those that are inherent in the choice of the atomic basis set and suggest that the present procedure may be useful in calculations on larger molecules.

IV. APPLICATION TO BENZENE AND BORAZINE

In this section, the QVO procedure is applied to benzene and borazine. The cc-pVTZ basis set has 264 basis functions for both molecules. Such calculations are now routine with P3 and other quasiparticle electron propagator methods.

The molecular geometries were taken from Ref. 6. Molecular symmetry was not exploited. Table III shows the results for valence ionization energies obtained with the P3 method using the cc-pVTZ basis set. Calculations with the full virtual space are used as a reference for accuracy. The

TABLE III. P3/cc-pVTZ ionization energies (eV) with 50% and 100% of original virtual orbital space rank.

Molecule	Orbital	50%	100%
Benzene	e_{1g}	9.362	9.402
	e_{2g}	12.166	12.302
	a_{2u}	12.321	12.384
	e_{1u}	14.362	14.466
	b_{2u}	15.000	15.066
	b_{1u}	15.636	15.757
	a_{1g}	17.197	17.314
Borazine	e''	10.290	10.318
	e'	11.682	11.825
	a_2''	12.847	12.906
	a_1'	13.926	14.037
	e'	15.079	15.152
	a_2'	14.872	14.929
	e'	17.848	17.905

data indicate that a 50% rank reduction of the virtual space introduces deviations of only 0.1 eV. At the same time, the QVO procedure reduces the disk demand to less than 20% of its original size. (About 6 Gbytes of disk were required for the calculations with the reduced virtual space.) Similar savings in computation time also were obtained. In benzene, the savings due to the reduction of the virtual space are comparable to those obtained by using abelian point-group symmetry in the calculation.

The data of Table III also indicate that the ionization energies calculated with a reduced virtual space have deviations from the results with unmodified orbitals[6] that depend only slightly on the final state. Despite the use of different virtual spaces for each transition energy, the quality of the calculations is maintained. The interpretation of ionization spectra is not affected adversely. It should be possible to approximately infer the results of a full virtual space calculation by extrapolating from a series of values that correspond to given percentages of virtual rank reductions.

V. CONCLUSIONS

Effective density difference matrices that correspond to electron binding energies in the diagonal, second-order approximation of the electron propagator may be used to reduce the rank of the virtual orbital space that is used in calculations with more accurate methods. Because the greatest demands for arithmetic operations and data storage in several electron propagator approximations depend cubically on the number of virtual orbitals, such rank reductions may facilitate otherwise infeasible calculations. The component steps and the organization of the associated algorithm have been described. This procedure has been implemented as a modification to the electron propagator programs in the GAUSSIAN 03 suite of programs.[17]

Numerical results are very encouraging. A reduction of the rank of the virtual orbital space by 50% leads to deviations of only 0.1 eV with respect to calculations that employ the full set of virtual orbitals. Such errors are less than those that are usually inherent in the choice of an atomic basis set. Arithmetic operation and data storage requirements for results of a given quality may be substantially diminished by the present procedure.

Elimination of virtual orbitals according to purely energetic criteria may lead to errors that are unacceptably large. Virtual orbitals with high energies may be important in the calculation of a given ionization energy. Therefore, an alternative to a purely energetic criterion for virtual orbital retention is needed to facilitate accurate electron propagator calculations on large molecules.

The present method generates virtual orbitals that are adapted separately for each valence ionization energy. Reduction of the rank of the virtual orbital space by a fixed percentage yields a consistent deviation with respect to reference calculations that employ the full set of virtual orbitals. The latter limit may be inferred from a sequence of calculations with differing percentage reductions of the virtual orbital space.

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