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Generalized overlap amplitudes using the extended Koopmans' theorem for Be

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Approximate generalized overlap amplitudes (GOAs), also called Feynman–Dyson amplitudes, have been calculated from a full configuration interaction (CI) wave function for the ground state of beryllium using the extended Koopmans' theorem (EKT). The GOAs were also calculated from the ground state CI wave function for Be and the ground state and excited state CI wave functions for Be^+ . The EKT GOAs are nearly identical to the corresponding CI GOAs for the lower 2S states of Be^+ and for the $\text{Be}^+ 1s2s^2$ state which has a large GOA occupation number. There are many CI GOAs for which there is not a corresponding EKT GOA. This may be due in part to the limited size of the basis set and to the inability to include natural spin orbitals with small occupation numbers in the EKT calculations. © 1995 American Institute of Physics.

INTRODUCTION

Orbital pictures and one-electron models have long contributed to our understanding of chemical bonding, but sometimes orbital pictures get lost in accurate models which account for electron correlation. It has recently been pointed out that generalized overlap amplitudes (GOAs), also called Feynman–Dyson amplitudes and Dyson orbitals, can provide a one-electron picture of chemical bonding in electron propagator methods.¹ They are useful in interpreting electron momentum spectroscopy experiments,² electron capture,³ electron scattering phenomena,⁴ photoionization,⁵ as well as molecular structure and bonding. The GOAs between the $(N-1)$ -electron states and the reference state of the N -electron system are defined by⁶

$$g_i(x) = m_i^{-1/2} \langle \Psi_i^{N-1} | \hat{\psi}(x) | \Psi^N \rangle. \quad (1)$$

The GOAs between the $(N+1)$ -electron states and the reference state of the N -electron system are given by

$$f_i(x) = m_i'^{-1/2} \langle \Psi_i^{N+1} | \hat{\psi}(x)^\dagger | \Psi^N \rangle. \quad (2)$$

The $\hat{\psi}(x)$ is the field operator and the coordinate x represents both space and spin coordinates. The factors $m_i^{-1/2}$ and $m_i'^{-1/2}$ serve to normalize the GOAs.⁷ The m_i can be interpreted as occupation numbers for the g_i . The m_i lie between 0 and 1 and they sum to the number of electrons. In general they are not the same as the natural spin–orbital (NSO) occupation numbers.

When the exact wave functions are used, the sets $\{g_i\}$ and $\{f_i\}$ together form a complete set.⁶ The $\{g_i\}$ in general are not orthogonal. It has been conjectured, though not proven, that the set $\{g_i\}$ is not a complete set. Whether the set $\{g_i\}$ is linearly dependent is still open to question and is related to the question of the existence of NSOs with zero occupation numbers.⁸

In this paper we are primarily interested in the g_i and will refer to these as the GOAs. The N -electron wave function can be written in terms of the g_i and the eigenfunctions of the $(N-1)$ -electron Hamiltonian:

$$\Psi^N(x_1, x_2, \dots, x_N) = \sum_i \Psi_i^{N-1}(x_1, x_2, \dots, x_{N-1}) \times \left(\frac{m_i}{N} \right)^{1/2} g_i(x_N). \quad (3)$$

Here the g_i can be viewed as expansion coefficients and are the best orbitals into which an electron can be added to form the N -electron state from the i th $(N-1)$ -electron state.

In a previous paper⁹ the long-range behavior of the GOAs was examined for the Li atom. Many of the GOAs are similar to the orbitals that are occupied in the SCF approximation if they have the same symmetry as one of the occupied orbitals. Even though GOAs with the same spin may have the same long-range exponential decay,^{10,11} they appear to have distinct exponential decays in the intermediate range.⁹ This holds out the possibility that they might be linearly independent, though not complete. Of course, in any calculation using a finite basis set they are linearly dependent since the number of $(N-1)$ -electron states exceeds the number of basis functions when $N > 2$.

The extended Koopmans' theorem (EKT)^{12–14} is a one-electron model for calculating ionization energies from many-electron correlated wave functions, and in principle from the exact wave function.¹⁰ The EKT has been shown to be exact for the lowest IP if the N -electron wave function is exact.^{15,16} Numerical calculations indicate that it may also be exact for some IPs besides the lowest one.^{17–19}

The extended Koopmans' theorem can be used to find approximate wave functions for the $(N-1)$ -electron system and therefore it can be used to calculate approximate GOAs. A relationship to obtain GOAs from the extended Koopmans' theorem has been given by Chipman.²⁰ The relationship between one-electron equations for the GOAs and the EKT equations has been shown by Day.⁷

THEORY

In this section we review some equations associated with the EKT and write the equations for the g_i in terms of the coefficients found from the EKT matrix equations.

In the EKT model, ionization can be viewed as the annihilation of an optimized orbital from the N -electron wave function to form an $(N-1)$ -electron wave function,^{12–14}

$$|\Psi_i^{N-1}\rangle = \hat{q}_i |\Psi^N\rangle. \quad (4)$$

The \hat{q}_i represent the best linear combination of annihilation operators to produce Ψ_i^{N-1} from Ψ^N . They have imbedded in them the appropriate coefficients to produce orthonormal Ψ_i^{N-1} . The \hat{q}_i and ionization energies are found by solving the matrix equations

$$(\mathbf{V} - \epsilon \mathbf{n}) \mathbf{c} = 0, \quad (5)$$

where the matrix \mathbf{V} is defined by

$$V_{ij} = -\langle \Psi^N | \hat{a}_j^\dagger [\hat{H}, \hat{a}_i] | \Psi^N \rangle, \quad (6)$$

and \mathbf{n} is defined by

$$n_{ij} = \langle \Psi^N | \hat{a}_j^\dagger \hat{a}_i | \Psi^N \rangle. \quad (7)$$

The \hat{a}_i^\dagger and \hat{a}_j are NSO creation and annihilation operators. The operators \hat{a}_j annihilate NSOs from the N -electron wave function to produce functions in the $(N-1)$ -electron space. The values $-\epsilon_i$ are approximations to ionization energies.

The matrix V will not, in general, be Hermitian unless the wave function Ψ^N is an eigenfunction of a model Hamiltonian such as the second-quantized Hamiltonian for a given orbital set. Such wave functions include full configuration interaction (CI) wave functions and multiconfigurational-self-consistent-field (MCSCF) wave functions, among others.

The metric matrix \mathbf{n} has the NSO occupation numbers, n_i , along the diagonal and zeros in off-diagonal elements. When \mathbf{n} contains occupation numbers that are very small Eq. (5) becomes numerically ill conditioned. It is sometimes necessary to omit terms in \mathbf{n} corresponding to n_i that have values below a certain threshold. Equation (5) can be transformed by canonical orthonormalization using $\mathbf{n}^{-1/2}$. With this transformation Eq. (5) can be written as

$$(\mathbf{V}' - \epsilon \mathbf{I}) \mathbf{c}' = 0. \quad (8)$$

The optimized annihilation operator can be written in terms of the solution of Eq. (8)

$$\hat{q}_i = \sum_j c'_{ji} n_j^{-1/2} \hat{a}_j. \quad (9)$$

Combining the field operator to generate the GOAs in Eq. (1) and the \hat{q}_i operator to generate Ψ_i^{N-1} in Eq. (4) gives

$$g_i^{\text{EKT}}(x) = m_i^{-1/2} \langle \Psi^N | \hat{q}_i^\dagger \hat{\psi}(x) | \Psi^N \rangle, \quad (10)$$

as shown by Chipman.²⁰ Using NSO expansions for both \hat{q}_i and $\hat{\psi}(x)$ we get

$$g_i^{\text{EKT}}(x) = m_i^{-1/2} \sum_j c'_{ji} n_j^{1/2} \chi_j(x). \quad (11)$$

The c' coefficients are the eigenvector solutions to Eq. (8). The NSO occupation numbers enter Eq. (11) with a positive $1/2$ power providing a weighting factor which is small for NSOs that have small occupation numbers. This is consistent with the observation that many GOAs appear to be similar to

TABLE I. The NSO occupation numbers. Numbers in parentheses for the p and d NSO occupation numbers refer to their spatial degeneracies.

| s | p | d |
|------------------------------|---------------------------------|---------------------------------|
| 0.998 163 | $0.294\,541 \times 10^{-1}$ (3) | $0.688\,609 \times 10^{-4}$ (5) |
| 0.909 468 | $0.353\,497 \times 10^{-3}$ (3) | $0.483\,698 \times 10^{-5}$ (5) |
| $0.187\,457 \times 10^{-2}$ | $0.435\,676 \times 10^{-4}$ (3) | $0.783\,823 \times 10^{-6}$ (5) |
| $0.495\,836 \times 10^{-3}$ | $0.129\,711 \times 10^{-4}$ (3) | |
| $0.212\,687 \times 10^{-4}$ | $0.144\,067 \times 10^{-5}$ (3) | |
| $0.625\,116 \times 10^{-5}$ | $0.232\,086 \times 10^{-7}$ (3) | |
| $0.102\,932 \times 10^{-5}$ | $0.924\,39 \times 10^{-12}$ (3) | |
| $0.331\,745 \times 10^{-6}$ | | |
| $0.773\,925 \times 10^{-7}$ | | |
| $0.402\,427 \times 10^{-7}$ | | |
| $0.105\,541 \times 10^{-7}$ | | |
| $0.677\,406 \times 10^{-9}$ | | |
| $0.824\,779 \times 10^{-10}$ | | |
| $0.126\,755 \times 10^{-11}$ | | |
| $0.924\,936 \times 10^{-12}$ | | |

the orbitals that are occupied in the SCF wave function if they have the same symmetry as one of the occupied orbitals.

The EKT GOAs are approximations to GOAs obtained from CI wave functions. Because the lowest ionization energy can be obtained very accurately using the EKT, we expect that the corresponding EKT GOA will also be very accurate.

CALCULATIONS AND RESULTS

A full CI wave function was calculated for Be using a basis set of $12s$, $8p$, and $3d$ primitive Gaussian orbitals.²¹ The basis set includes the $x^2 + y^2 + z^2$ combinations from the d orbitals. The total energy calculated using this basis set is $-14.658\,40$ a.u. The ground state wave function of Be and the EKT GOAs were calculated using the GAMESS²² program. The 2S and 2P excited state wave functions of Be^+ were computed in the same basis set and the GOAs corresponding to these excited states were calculated using the MELD programs.^{23,24}

Ionization energies and the corresponding normalized GOAs were calculated using the EKT, Eqs. (8) and (11), and from the excited state CI wave functions of Be^+ using Eq. (1). We refer to these two sets of GOAs as the EKT GOAs and the CI GOAs, respectively.

The size of the $(N-1)$ -electron space in the EKT calculation is the same as the size of the space spanned by the NSOs retained for the calculation. Twelve s -type NSOs of each spin type were used in the EKT calculation so the $(N-1)$ -electron basis set size is 12 for the 2S states of Be^+ , compared with the 7670 configurations in the CI wave function using D_{2h} symmetry. The accuracy and number of IPs calculated using the EKT method depends on the number of NSOs included in the calculation. Solutions to Eq. (8) which include all of the 51 NSOs were numerically unstable in the sense that the variation theorem was violated for some IPs. It was therefore necessary to omit NSOs that have an occupation number below a certain value δ . The NSO occupation numbers are listed in Table I. The smallest NSO occupation numbers are about 1×10^{-12} .

TABLE II. The *s*-type EKT IPs and GOA occupation numbers for values of the NSO cutoff δ . Values are omitted for GOAs corresponding to IPs>4.7 a.u.

| δ (Be ⁺ state) | 1.0×10 ⁻⁵ | | 1.0×10 ⁻⁷ | | 1.0×10 ⁻⁹ | |
|-------------------------------------|----------------------|--------|----------------------|--------|----------------------|--------|
| | IP | m | IP | m | IP | m |
| (1s ² 2s) | 0.3424 | 0.8408 | 0.3420 | 0.8886 | 0.3420 | 0.8884 |
| (1s ² 3s) | 0.8177 | 0.0202 | 0.7646 | 0.0217 | 0.7479 | 0.0204 |
| (1s ² 5s) | ... | ... | ... | ... | 1.0352 | 0.0021 |
| (1s ² 6s) | ... | ... | 1.3834 | 0.0009 | ... | ... |
| (1s ² 7s) | ... | ... | ... | ... | 1.7724 | 0.0004 |
| (1s ² 8s) | ... | ... | ... | ... | 3.2425 | 0.0035 |
| (1s2s ²) | 4.6829 | 0.9864 | 4.6540 | 0.9364 | 4.6941 | 0.9850 |

Table II shows the results of EKT calculations for values of δ ranging from 1.0×10⁻⁵ to 1.0×10⁻⁹. When δ =1.0×10⁻⁵ the EKT method produces only 3 IPs less than 4.7 a.u. The EKT IPs and GOAs corresponding to the Be⁺ 1s²4s through 1s²8s are missing. When δ is reduced to 1.0×10⁻⁷ an additional EKT IP corresponding to the Be⁺ 1s²6s state is calculated. When δ is further reduced to 1×10⁻⁹ the EKT IPs corresponding to Be⁺ 1s²5s and 1s²7s are present, but the ones for 1s²4s and 1s²6s are missing. These could likely be calculated by including NSOs with smaller occupation numbers in the EKT calculations, and by increasing the numerical accuracy of the calculations. Greater numerical accuracy would allow more NSOs with smaller occupation numbers to be included in the calculation. As shown in Table II, this would likely produce IPs which are missing in the current calculations, and it would likely improve the accuracy of the calculated IPs.

Comparisons between the EKT GOAs and the CI GOAs were made with EKT GOAs calculated using a δ =1.0×10⁻¹⁰. This omits three *s*-type and one *p*-type NSOs. Setting the cutoff δ to 1.0×10⁻¹¹, or lower, resulted in EKT IPs which were variationally too low.

Overlaps between the *s*-type EKT GOAs and the *s*-type CI GOAs are listed in Table III and for *p*-type GOAs are listed in Table IV. The overlap between the first *s*-type EKT GOA and the first *s*-type CI GOA is 1 to the limit of the numerical accuracy of the calculations. This is consistent with previous analyses of the exactness of the EKT for the lowest IP. The values of the overlaps are used to identify the

TABLE IV. Overlap of *p*-type EKT GOAs with CI GOAs. The asterisk indicates that an EKT GOA is matched with the corresponding CI GOA.

| EKT | | | |
|----------|-------------------------------|---------------------------|---------------------------|
| | g_i (Be ⁺ state) | $p1$ (1s ² 2p) | $p2$ (1s ² 3p) |
| <i>C</i> | $p1$ (1s ² 2p) | 1.000 000* | 0.9366 |
| <i>I</i> | $p2$ (1s ² 3p) | 0.9571 | 0.9948* |
| | $p3$ (1s ² 4p) | 0.9686 | 0.9936 |
| | $p4$ (1s ² 5p) | 0.9732 | 0.9913 |

EKT GOAs with CI GOAs. Based on the ionization energies in Table IV and the shapes in Figs. 1 and 2, the first EKT GOA and the first CI GOA are 2s like. The sixth EKT GOA and the eighth CI GOA are 1s like. The second and third *s*-type EKT GOAs have overlaps with the first CI GOA greater than 0.9 indicating that they are also 2s like and the second through fifth CI GOAs have overlaps ranging from 0.89 to 0.97 with the first GOA indicating they are 2s like. The fourth EKT GOA has an overlap of 0.58 with the first CI GOA and 0.69 with the eighth CI GOA indicating it is intermediate between the 1s- and 2s-like GOAs. Likewise the sixth and seventh CI GOAs appear to be intermediate between the 1s- and 2s-like GOAs with the seventh one looking a little more like the 1s-like GOA. The fifth EKT GOA is 1s like. The EKT GOAs for *i*>6 are not listed because the corresponding EKT IPs are far above the 1s IP listed, whereas there are a number of CI IPs which are only slightly higher than the 1s IP.

The IPs and GOA occupation numbers are listed in Table V for the EKT and CI GOAs along with their overlaps. The six *s*, two *p*, and one *d* EKT GOAs are arranged to be opposite their CI GOA counterparts as identified by the overlaps in Table III. Experimental IPs and IPs from Ref. 21 from the multiconfigurational spin tensor electron propagator (MCSTEP) method and the repartitioned MCSTEP (RM-STEP) method are listed for comparison. The lowest EKT IP is equal to the lowest CI IP to all places reported. The EKT IPs for the transitions into the Be⁺ 1s²2s, 1s²3s, and 1s²2p states are comparable to the RMCSTEP and the EKT values into the 1s²2s and 1s²2p states also agree well with experiment. Even though the overlap of the EKT GOA and the CI GOA corresponding to the Be⁺ 1s2s² state is 1 to 5 decimal

TABLE III. Overlap of *s*-type EKT GOAs with CI GOAs. The asterisk indicates that an EKT GOA is matched with the corresponding CI GOA.

| EKT | | | | | | | | |
|----------|-------------------------------|---------------------------|---------------------------|---------------------------|---------|---------------------------|---------------------------|-----------|
| | g_i (Be ⁺ state) | 2s like | | | mixed | 1s like | | |
| | | $s1$ (1s ² 2s) | $s2$ (1s ² 3s) | $s3$ (1s ² 5s) | | $s5$ (1s ² 8s) | $s6$ (1s2s ²) | |
| <i>C</i> | 2s like | $s1$ (1s ² 2s) | 1.000000* | 0.9665 | 0.9193 | 0.5832 | 0.06673 | 0.001098 |
| | | $s2$ (1s ² 3s) | 0.9671 | 0.999994* | 0.9873 | 0.6737 | 0.09573 | 0.01426 |
| | | $s3$ (1s ² 4s) | 0.9471 | 0.9974 | 0.9962 | 0.7009 | 0.1131 | 0.02787 |
| | | $s4$ (1s ² 5s) | 0.9352 | 0.9940 | 0.9987* | 0.7153 | 0.1245 | 0.03739 |
| | | $s5$ (1s ² 6s) | 0.8913 | 0.9737 | 0.9973 | 0.7648 | 0.1754 | 0.08317 |
| <i>I</i> | mixed | $s6$ (1s ² 7s) | 0.7509 | 0.8648 | 0.9273 | 0.8960 | 0.3949 | 0.2988 |
| | | $s7$ (1s ² 8s) | 0.2530 | 0.3216 | 0.4017 | 0.9086 | 0.94009 | 0.8982 |
| | 1s like | $s8$ (1s2s ²) | 0.0002936 | 0.01357 | 0.06554 | 0.6917 | 0.9944 | 0.999997* |

TABLE V. Ionization energies and occupation numbers for GOAs calculated from the EKT and CI methods for Be, along with experimental values and values from Ref. 21.

| Be ⁺ | EKT | | | | CI | | | Expt. IP | MCSTEP ^c IP | RMCSTEP ^c IP |
|--------------------|-----|--------|-------------------------|-----------|-----|--------|-------------------------|---------------------|---------------------------|----------------------------|
| | GOA | IP | m | Overlap | GOA | IP | m | | | |
| 1s ² 2s | s1 | 0.3420 | 0.8884 | 1.000 000 | s1 | 0.3420 | 0.8883 | 0.3426 ^a | 0.342 | 0.341 |
| 1s ² 3s | s2 | 0.7478 | 0.2039×10 ⁻¹ | 0.999 994 | s2 | 0.7436 | 0.1919×10 ⁻² | 0.7446 ^a | 0.8482 | 0.7427 |
| 1s ² 4s | | | | | s3 | 0.8681 | 0.1509×10 ⁻² | 0.8687 ^a | | 0.8666 |
| 1s ² 5s | s3 | 1.0318 | 0.2162×10 ⁻² | 0.9987 | s4 | 0.9387 | 0.1162×10 ⁻² | 0.9228 ^a | | |
| 1s ² 6s | | | | | s5 | 1.1797 | 0.7607×10 ⁻³ | 0.9511 ^a | | |
| 1s ² 7s | s4 | 1.7615 | 0.3652×10 ⁻³ | 0.8960 | s6 | 1.7430 | 0.1387×10 ⁻³ | 0.9678 ^a | | |
| 1s ² 8s | s5 | 3.2129 | 0.3274×10 ⁻² | 0.9401 | s7 | 2.8528 | 0.7930×10 ⁻⁴ | | | |
| 1s2s ² | s6 | 4.6936 | 0.9851 | 0.999 997 | s8 | 4.5353 | 0.760852 | 4.5408 ^b | | |
| 1s ² 2p | p1 | 0.4888 | 0.2922×10 ⁻¹ | 1.0000 | p1 | 0.4881 | 0.2917×10 ⁻¹ | 0.4881 ^a | 0.4932 | 0.4899 |
| 1s ² 3p | p2 | 1.0388 | 0.5559×10 ⁻⁴ | 0.9948 | p2 | 0.7819 | 0.4324×10 ⁻⁴ | 0.7823 ^a | 0.9588 | 0.7809 |
| 1s ² 4p | | | | | p3 | 0.8835 | 0.1650×10 ⁻⁴ | 0.8837 ^a | | 0.8816 |
| 1s ² 5p | | | | | p4 | 0.9342 | 0.1571×10 ⁻⁴ | 0.9302 ^a | | |
| 1s ² 3d | d1 | 0.8516 | | 0.9995 | d1 | 0.7973 | | 0.7894 | | 0.7945 |

^aReference 25.^bReference 26.^cReference 21.

places, the EKT IP of 4.6936 a.u. is only slightly better than the Koopmans' theorem IP of 4.7325 a.u. in the same basis.

The highest occupied EKT GOA is *s*₆ corresponding to removal of a 1s electron from Be in the Koopmans' theorem model. The eighth *s*-type CI GOA also has a high occupation number, 0.7608, although considerably less than the sixth *s*-type EKT GOA.

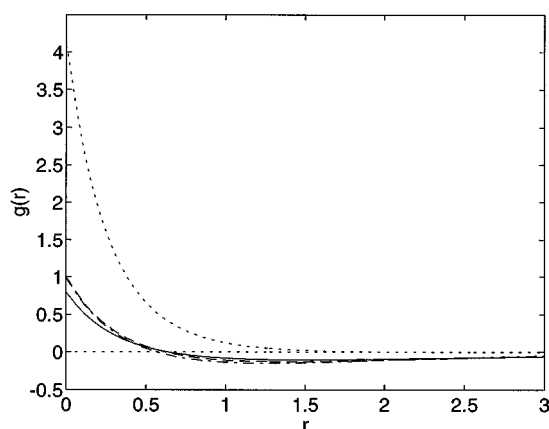
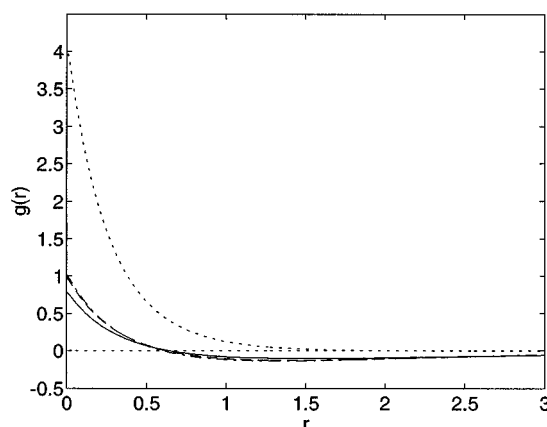
The EKT IP for the *d* GOA is significantly above the CI value. Although the *d* basis set is small, a calculation which included 7*d* orbitals produced a *d* IP of 0.84 a.u. which is only marginally better than the value of 0.85 a.u. in Table V. In the extended *d* basis only three *d* NSOs had occupation numbers above the cutoff value of 1.0×10⁻¹⁰. The poor quality of the *d* IP may be due to the inability to include NSOs with small occupation numbers in the EKT calculations.

The *s*-type EKT GOAs 1, 2, 3, and 6 are shown in Fig. 1 and the *s*-type CI GOAs 1, 2, 3, and 8 are shown in Fig. 2. There is essentially no difference, visually, between the four

EKT GOAs and the corresponding four CI GOAs. The first two *p*-type EKT GOAs are shown in Fig. 3 and the first four *p*-type CI GOAs are shown in Fig. 4. The first *p*-type CI GOA is quite different from the others shown. The first *p*-type EKT GOA is nearly identical to the first *p*-type CI GOA. In Fig. 5 the *d*-type EKT GOA is compared with the *d*-type CI GOA. Although the IPs are significantly different, the GOAs are quite similar. Because of its higher IP the *d*-type EKT GOA decays more rapidly for *r*>4 a.u. than the *d*-type CI GOA.

DISCUSSION

The GOAs can be used to provide an orbital interpretation of complex correlated wave functions. The EKT can be used to accurately calculate GOAs from MCSCF wave functions or from full CI wave functions. The EKT GOAs are nearly identical to the CI GOAs for the lowest ionic states of Be⁺ and for the states which have high GOA occupation numbers. Many (*N*−1)-electron states appear to be acces-

FIG. 1. *S*-type EKT GOAs. *g*₁ is solid, *g*₂ is long dashed, *g*₃ is short-dash-long dashed, *g*₆ is short dashed.FIG. 2. *S*-type CI GOAs. *g*₁ is solid, *g*₂ is long dashed, *g*₃ is short-dash-long dashed, *g*₈ is short dashed.

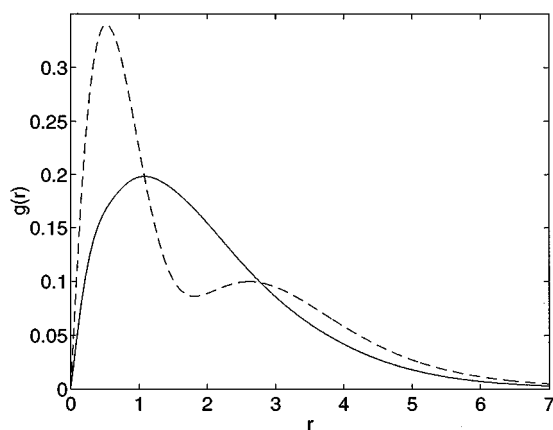


FIG. 3. *P*-type EKT GOAs. g_1 is solid, g_2 is dashed.

sible using the EKT, and calculating GOAs with the EKT offers a convenient way of providing an orbital interpretation for MCSCF wave functions. The first three $2s$ like, the first two $2p$ like and the $1s$ like EKT GOAs appear visually similar to the corresponding CI GOAs. This visual examination is verified by the fact that the overlaps between these EKT GOAs and the corresponding CI GOAs are close to one.

Some of the Be^+ states appear to be missing in the EKT calculations. For example the $^1S(1s^2 2s^2) \rightarrow ^2S(1s 2s^2)$ and $^1S(1s^2 2s^2) \rightarrow ^2P(1s^2 2p)$ are present in our reported EKT calculations, but the $^1S(1s^2 2s^2) \rightarrow ^2S(1s^2 4s)$ is not. The calculation of such transitions might be possible with larger basis sets if we could solve the numerical difficulties associated with Eqs. (5) and (8) when NSOs with small occupation numbers are included in the calculations. It is not yet known for certain whether this is because the Φ_i^{N-1} corresponding to NSOs with zero occupation numbers are needed, or whether these occupation numbers are just so small that they are beyond the limits of the accuracy of the numerical calculations. It is possible that it is merely because the calculations are just beyond the limits of accuracy of the numerical procedures. There is recent evidence that the NSO occupa-

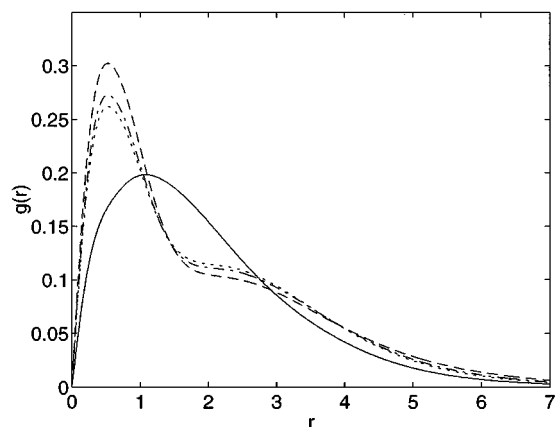


FIG. 4. *P*-type CI GOAs. g_1 is solid, g_2 is long dashed, g_3 is short-dash-long dashed, g_4 is short dashed.

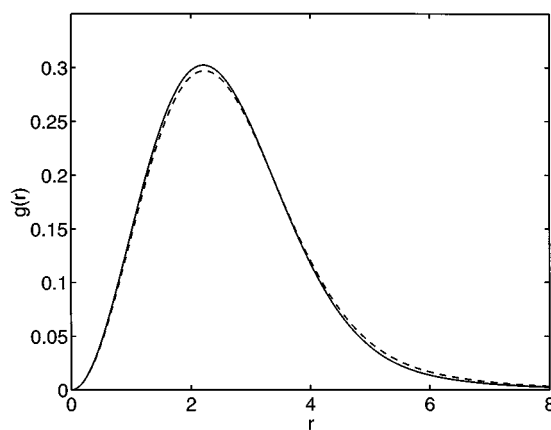


FIG. 5. The first *d*-type GOA. The solid line is the EKT GOA and the dashed line is the CI GOA.

tion numbers for ground state wave functions might not be identically zero,^{8,9} but just get very small, except for very rare cases where they might be zero by symmetry. Very small NSO occupation numbers cause Eqs. (5) and (8) to become numerically ill conditioned. This imposes practical limitations on the accessibility of IPs and GOAs from the EKT for some ionic excited states with the limits of numerical accuracy used herein.

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