

N86 - 30377**On the Electron Affinity of the oxygen atom**

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Abstract

The electron affinity of oxygen is computed to be 1.287 eV, using 2p electron full CI wave functions expanded in a 6s5p3d2f Slater-type orbital basis. The best CASSCF-MRCI result including only 2p correlation is 1.263 eV. However, inclusion of 2s intrashell and 2s2p intershell correlation increases the computed EA to 1.290 at the CASSCF-MRCI level. At the full CI basis set limit, the 2s contribution to the electron affinity is estimated to be as large as 0.1 eV. This study clearly establishes the synergistic effect between the higher excitations and basis set completeness on the electron affinity when the 2s electrons are correlated.

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I. Introduction

The calculation of the electron affinity (EA) of the oxygen atom has proved to be a challenging task [1-5]. A noteworthy study of atomic correlation and its effects on calculated electron affinities is the work of Sasaki and Yoshimine [1] (SY). Using extremely large Slater basis sets, they were able to estimate the SDCI basis limit for the electron affinity of oxygen as 1.041 eV, which is substantially less than the experimental value [6] of 1.462 eV. This work indicated that earlier pair-correlation calculations [7-10] obtained electron affinities in fortuitously good agreement with experiment owing to a cancellation between atomic basis set incompleteness and the excess energy from neglected pair-pair interaction energies. By including selected triple and quadruple excitations, SY obtained an electron affinity of 1.17 eV including only L shell correlation. SY also showed that correlation of the 1s electrons makes a very small contribution to the EA.

The study of Botch and Dunning [2] (BD), demonstrates that the differential higher excitation contribution to the EA is more efficiently accounted for by an MCSCF multi-reference CI procedure, MRCI, than by using selected triple and quadruple excitations from an SCF reference. Their MCSCF calculation was restricted to double excitations out of the 2p into 2p' correlating orbitals, and yielded an EA of 0.46 eV, about 1 eV improvement over the Hartree-Fock limit of -0.54 eV. When all single and double excitations from this MCSCF reference were included, they obtained an electron affinity of 1.09 eV. This value is less than that of SY owing to the much smaller basis set employed, but indicates a considerably larger contribution from higher excitations. The most important correlation contribution was observed to arise from 2p→2p' excitations.

The first systematic study of the EA of oxygen correlating only the 2p electrons was given by Bauschlicher [3]. Using a large (6s6p3d2f) Slater-type orbital (STO) basis that is within about 0.05 eV of the SDCI basis set limit value, a CASSCF calculation with the 2p and 2p' orbitals in the active space was performed. This CASSCF yields an EA of 0.59 eV which is similar to the EA from the MCSCF calculation of Botch and Dunning [2]. More extensive correlation was included via a second-order CI including only the 2p electrons. The second-order CI yields an

EA of 1.26 eV, which is larger than that of SY, but still in error by 0.2 eV. When the MCSCF and MRCI reference spaces were expanded to include the 3d shell, the EA increased to only 1.28 eV.

Recently, Feller and Davidson [4] (FD) calculated the EA of O using an MCSCF-MRCI approach. Unlike Bauschlicher [3], FD explicitly included the 2s in both the MCSCF and multi-reference CI calculations. The gaussian type orbital (GTO) basis used by FD is within 0.02 eV of the SY SDCI limit EA. The results of FD parallel those of Bauschlicher, and their best EA is 1.29 eV, or 1.32 eV if an estimate of higher excitations is made. This work suggests that 2s does not have a differential correlation contribution to the EA, and therefore either the differential contribution of higher excitations to the EA converges very slowly with basis set, or else none of the MCSCF-MRCI studies to date have properly accounted for this 2s contribution. This latter possibility seems unlikely considering the stability of the EA to further improvements in the treatment, e.g. including the 3d shell in the active space. However, Raghavachari [5] finds with a comparable basis set that a coupled cluster doubles (CCD) calculation with a correction for single and triple excitations yields an EA of 1.41 or 1.36 eV, depending upon the approximation used for the single and triple excitations.

It has recently become possible to perform very large full CI calculations which can be analyzed to separate the effect of higher excitations from basis set incompleteness. This is a result of: (i) Siegbahn's realization [11] that the full CI procedure can be vectorized in terms of matrix multiplies, (ii) Knowles and Handy's suggestion [12] that the Siegbahn approach be changed to determinants from configuration state functions, thus eliminating the IO bottleneck associated with the formula file, and (iii) the delivery of the CRAY 2 which allows very large CI expansions because of its extremely large memory.

In this work we report full CI calculations of the EA of O atom, and compare these results to those obtained using an MCSCF-MRCI approach. One of the goals of the present study is to decompose the remaining error in the EA into effects of basis set incompleteness, higher excitations not accounted for by the CASSCF-MRCI treatment, and to contributions from correlating the 2s electrons. In addition, we report on our initial attempts to compute the EA using Green's function Monte

Carlo methods [13]. This approach seems particularly relevant to the EA affinity problem since it is potentially capable of accounting for all of the electronic correlation energy. However, technical problems make such calculations difficult at present for systems with this many electrons.

Section II contains a brief description of the methods and basis sets employed in this study. Section III contains an analysis of the full CI and CASSCF-MRCI calculations. Section IV contains a description of the Monte Carlo calculations. The conclusions are given in Section V.

II. Methods

In our theoretical calculations we employ a 6s5p valence Slater-type orbital set obtained by combining six s functions optimized for O, and five p functions optimized for O⁻ [14]. The total SCF energy of the 6s5p basis is only 0.0001 Hartree above the numerical Hartree Fock (NHF) energy; this can be compared to, for example, an uncontracted 12s7p GTO basis set [15] which has an error six times larger. However, both O and O⁻ are affected similarly by basis set limitations, so the EA is at the HF limit.

To the 6s5p valence basis we construct a small basis by adding one 3d function with an exponent of 2.66 and a larger 3d2f polarization set with exponents of 4.0, 2.8284 and 2.0 for the three 3d functions and exponents of 4.06 and 2.87 for the two 4f functions. The exponents were optimized by Bauschlicher [3], under an even-tempered constraint, by minimizing the mean of the O and O⁻ energies at the SDCI level, with only the 2p electrons correlated. However, the optimal exponents are not significantly different for O and O⁻ and hence little bias is expected for the larger polarization set.

Several zeroth-order references are used. The simplest is the SCF, in which symmetry and equivalence restrictions are imposed. For the MCSCF reference spaces, we use the CASSCF approach. In the smaller CASSCF only the 2p electrons are active, and are distributed in the 2p and 2p' orbitals; this CASSCF wave function is denoted CASSCF(2p). Since the question of the correlation effect of the O 2s is of interest, a second CASSCF wave function is also used, CASSCF(2s2p),

which includes the 2s as active and adds a 2s' correlating orbital.

In order to analyze the various correlation effects, more extensive correlation is added to the zeroth-order references in several ways. To separate the contribution to the EA from the 2s and 2p electrons, only the 2p electrons are correlated in some calculations, denoted CI(2p), while in others both the 2s and 2p are correlated, denoted CI(2s2p). For the SCF reference, only single reference SD CI calculations, or full CI calculations, FCI, are performed; the calculations are denoted CI(SCF,2s2p), for a single reference CI calculation (using SCF orbitals) which correlated the 2s and 2p electrons, or FCI(2p) for a full CI calculation which correlates only the 2p electrons. For the single reference CI calculations, we use the Davidson correction [16] (denoted +Q) to estimate the importance of quadruple excitations. For the CASSCF optimized orbitals, all calculations consist of single and double excitations from all of the configurations in the CASSCF calculation. For these calculations the notation indicates the origin of the orbitals and which electrons are correlated. Thus CI(CASSCF(2p),2s2p) denotes a calculation using orbitals optimized in a CASSCF(2p) calculation, and which includes single and double excitations out of the 2s and 2p orbitals in all configurations in the CASSCF(2p) wave function, while CI(CASSCF(2p),2p) involves the same orbitals and same references, but the 2s electrons are not correlated.

III. Results and discussion

The improvement of the electron affinity with enhancements of the polarization basis at the CI(SCF,2p) level is shown in Table I. These results using the 6s6p valence basis [3] are essentially unchanged if the valence basis is replaced by the 6s5p set used this study. The three d functions contribute a substantial 0.338 eV at this level, whereas the two f functions contribute 0.055 eV. For the 6s6p3d2f STO basis, the CI(SCF,2s2p) EA is 0.993eV (0.991 eV, for the 6s5p3d2f STO basis). This is about 0.05 eV less than the Sasaki and Yoshimine [1] CI(SCF,2s2p) EA of 1.041 eV, which should be near the basis set limit at this level. Feller and Davidson find a very similar CI(SCF,2s2p) EA using a 4d2f GTO basis. They also add a single g function, which is not optimized; this increases the CI(SCF,2s2p) EA by 0.037 eV, but increases the CI(CASSCF(2s2p),2s2p) EA by only 0.019 eV. The optimization

[3] of the d and f polarization function shows that the O energy is more sensitive to the choice of exponents than is O^- . Thus any error in the choice of the polarization function exponents tends to lead to too large an EA. Therefore we conclude that the 0.037 eV g function contribution is too large, and that 0.02 eV is probably a better estimate, with the saturation of the d and f spaces being of about the same importance.

The EA at various levels of correlation treatment using the 6s5p1d and 6s5p3d2f STO bases are summarized in Table II. Consider first the 6s5p1d basis set results where we have been able to perform the FCI(2s2p) calculation. The difference of 0.13 eV between the CI(SCF,2p) and CI(SCF,2s2p) electron affinities suggests a substantial reduction from 2s correlation. However, the reduction from including 2s correlation is only 0.085 eV if a correction is added for quadruple excitations. At the full CI level this reduction is only 0.027 eV. Clearly the importance of including the 2s changes markedly with increasing excitation level.

Since certain classes of higher excitation can be included efficiently using the MCSCF-MRCI approach, we next considered calculations from a CASSCF reference. When only 2p correlation is included, the CI(CASSCF(2p),2p) EA is only 0.011 eV less than the FCI value. If the 2s correlation is included for this choice of reference space, CI(CASSCF(2p),2s2p), the EA of 1.025eV is 0.034 eV less than the FCI value. If the same orbitals are used, but the CI reference space is increased to include all distributions of the 2s and 2p electrons in the 2s, 2p and 2p' orbitals, the EA is increased by only 0.003 eV. Thus to improve the computed EA, more orbitals must be included in the CASSCF orbital space and CI reference space. While the inclusion of the 2s electrons and the 2s' orbital in the CASSCF improves the CASSCF(2s2p) EA by 0.157 eV, relative to the CASSCF(2p) EA, the CI(CASSCF(2s2p),2s2p) EA is only 0.011 eV larger than the CI(CASSCF(2p),2s2p) EA, and is thus still in error by 0.023 eV.

The importance of higher excitations is considerably enhanced for the larger 6s5p3d2f basis. Including 2s correlation in the SCF reference SDCl decreases the EA by only 0.073 eV, and by only 0.017 eV when the Davidson correction for unlinked quadruples is added. The same coupling of basis set effects and the importance of higher excitations is illustrated by the difference between the CI(SCF,2p) and the

FCI(2p) electron affinities, which is 0.223 eV for the 6s5p3d2f STO basis and 0.183 eV for the 6s5p1d STO basis. The difference between the CI(CASSCF(2p),2p) and FCI(2p) EA also increases with the basis set improvement, being 0.024 eV for the larger basis compared to 0.011 eV for the 1d basis set. The difficulty of fully accounting for the effect of higher excitations is much more pronounced when the 2s electrons are correlated. For example, Feller and Davidson using a comparable basis obtain essentially the same CI(SCF,2s2p) EA, but their selected-reference MRCI calculation, based on CASSCF(2s2p) orbitals and correlating 2s and 2p, obtains 1.229 eV, compared to our CI(CASSCF(2s2p),2s2p) result of 1.290 eV. Thus the FD selection of references compared to our use of all CASSCF configurations as CI references has a substantial effect, even for a coefficient selection threshold of 0.01. Note that the CI(CASSCF(2s2p),2s2p) calculation for O^- in the 6s5p3d2f basis consists of all single and double excitations from 588 CSF's yielding a total 545,952 CSF's in D_{2h} symmetry. The motivation for reference selection is clearly evident, but leads to ambiguities for further improvements in the CASSCF treatment. For example, inclusion of the 3d orbital in the CASSCF treatment makes some selection of the CI references mandatory to keep the computations tractable. The relatively small affect of this extension is difficult to assess considering the effect of reducing the CI reference space.

The positive contribution of the 2s correlation at the CASSCF-MRCI level using the 6s5p3d2f basis is consistent with the trends observed at the CI(SCF) and CI(SCF)+Q levels as the basis set is improved. The contribution of the 2s correlation increases but is more difficult to account for as the basis set size is increased. At present, we are unable to perform the FCI(2s2p) calculations for the 6s5p3d2f basis set, since this involves an expansion consisting of 488 million determinants and about 4 billion intermediate states. However, the FCI(2s2p) EA can be estimated assuming that the difference CI(CASSCF(2p),2s2p)-FCI(2s2p) or CI(CASSCF(2s2p),2s2p)-FCI(2s2p) increases at the same rate as the difference CI(CASSCF(2p),2p)-FCI(2p) with basis set improvements. From the CI(CASSCF(2p),2s2p) calculation, we estimate the EA to be 1.35 eV, and from the CI(CASSCF(2s2p),2s2p) calculations we estimate 1.34 eV. These are probably underestimates, because the importance of higher excitations increases faster for

the FCI(2s2p) wave function than for FCI(2p) wave function. Thus, the FCI(2s2p) EA in the 6s5p3d2f could easily be as large as 1.36 eV. The remaining error of 0.1 eV can be rationalized in terms of the synergistic effect of basis set incompleteness and the contribution of higher excitations. That is, a basis set incompleteness error of 0.05 eV at the SDCl level becomes twice as large at the FCI(2s2p) level. These arguments also imply a relatively large positive differential contribution of the 2s correlation at the FCI level of 0.07 eV in the 6s5p3d2f basis, and quite possibly 0.1 eV in a complete one-particle basis.

Our theoretical results are reasonably consistent with a recent study of the EA of oxygen using Moller-Plesset perturbation theory by Raghavachari [5]. In particular, the value of 1.36 eV obtained by performing coupled-cluster calculations including all double substitutions, augmented by an estimate of the contributions of single and triple substitutions from the CCD wave function, CCD+ST(\dot{C} CD), is in good agreement with our FCI(2s2p) result. When the ST contribution is estimated from fourth-order Moller Plesset theory, CCD+ST(MP4), the value of 1.41 eV is probably too large. It would, however, be of considerable interest to see a more exact comparison of CCD calculations and the full CI results. This would resolve whether the excitations neglected in CCD make only a small contribution or whether the good agreement results from a cancellation of errors.

IV. Green's Function Monte Carlo

Although our full CI calculations give insight into what the computational requirements are for computing an electron affinity of oxygen with chemical accuracy, we presently cannot perform these calculations. Since the EA and the differential correlation energy (of 2.0 eV), are not expected to converge more rapidly than the total valence correlation energy, a calculation accounting for over 95% of the valence correlation energy is required to produce an EA to within 0.1 eV. Therefore, methods such as released node Green's function Monte Carlo [13], that can in principle account for all of the correlation energy, would seem to be especially appropriate for this problem.

Using a vectorized implementation of Green's function Monte Carlo on the Cyber-205, we describe here our initial attempts to compute the EA of oxygen

in collaboration with David Ceperley. The trial wavefunction used to guide the random walk consisted of a Slater determinant times a pair correlation function (Slater-Jastrow). The trial function only affects the statistical error of the energy, and not its limiting value. The atomic orbitals were determined from an SCF calculation using a 4s3p STO basis set. The EA computed at the fixed node level is 1.137 ± 0.063 eV. The nodal release procedure [17] employed, however, did not converge. The calculation was still far from convergence (especially for oxygen) after 42 generations [13,17]. It is impractical to continue the calculation further as the expectation values would become increasingly noisy and the total number of walks grows geometrically. This indicates that either a substantially better trial function is required, that is, the nodes need to be more accurately positioned by the trial function so that the relaxation to the correct nodes occurs more quickly, or that a more efficient nodal release procedure is required. We conclude that it is presently not feasible to compute an accurate EA for a system as heavy as oxygen using released node Green's function Monte Carlo. We present this problem as a challenge to future developments of the method.

Recently Barnett, Reynolds and Lester [18] reported a calculation of the EA of fluorine using fixed-node Monte Carlo. They obtained over 90% of the correlation for both the neutral and the anion, and an electron affinity of 3.45 ± 0.11 eV in excellent agreement with experiment. A single determinant, constructed with a double-zeta basis set, multiplied by electron-electron and electron-nuclear Jastrow functions were used as importance functions. These results contradict our experience with oxygen and the concept that methods which obtain 90% of the total correlation energy, such as CASSCF-MRCI, should yield 90% of the differential correlation contribution to the EA, which should lead to an error of about 0.2 eV for the EA of both O and F. Perhaps their trial function fortuitously places the nodes better for F^- , or some bias is introduced by the extrapolation to a zero time step.

V. Conclusions.

The CASSCF-MRCI and full CI calculations reported here show that higher excitations become more important as the one-particle basis set is improved. At high levels of correlation treatment, correlation of the 2s electrons makes a positive

contribution to the electron affinity of oxygen. In fact, we estimate that at the full CI basis set limit the 2s contribution could be as large as 0.1 eV. Reduction of the CASSCF reference space from which the MRCI is carried out is found to significantly affect the electron affinity, even for a selection threshold of 0.01 on the coefficients. Our attempts to compute a quantitative electron affinity for oxygen using both fixed-node and released-node Monte Carlo was not very successful. It is hoped that future developments in the released node procedure will significantly improve the applicability of Monte Carlo methods to systems as heavy as oxygen.

Acknowledgement.

The authors would like to acknowledge the contribution of David Ceperley for his help in implementing the Green's Function Monte Carlo (GFMC) method at NASA/Ames, and for his contribution on the calculations on O/O^- using GFMC. The authors are grateful for early access to the CRAY 2 and helpful advice from the NAS project.

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Table I. The computed EA as a function of the addition of polarization functions, for the CI(SCF,2p) level, in eV, taken from Reference 3.

Basis	EA
6s6p	0.676
1d	0.912
2d	0.996
3d	1.014
3d1f	1.047
3d2f	1.069
NHF	-0.54
EXP	1.462 ^a

^a Reference 6.

Table II. Summary of computed EA's, in eV.

Calculation	EA
	valence basis
NHF	-0.54
SCF 6s5p	-0.54
	6s5p1d
CI(SCF,2p)	0.903
CI(SCF,2p)+Q	1.042
CI(CASSCF(2p),2p)	1.075
FCI(2p)	1.086
CI(SCF,2s2p)	0.771
CI(SCF,2s2p)+Q	0.956
CI(CASSCF(2p),2s2p)	1.025 ^a
CI(CASSCF(2s2p),2s2p)	1.036
FCI(2s2p)	1.059
	6s5p3d2f
CI(SCF,2p)	1.064
CI(SCF,2p)+Q	1.217
CI(CASSCF(2p),2p)	1.263 ^b
FCI(2p)	1.287
CI(SCF,2s2p)	0.991
CI(SCF,2s2p)+Q	1.200
CI(CASSCF(2p),2s2p)	1.277
CI(CASSCF(2s2p),2s2p)	1.290
EXP	1.462 ^c

^a If the CI calculations are modified to include single and double excitations from all possible distributions of the 2s and 2p electrons among the 2s, 2p and 2p' orbitals the EA is increased to 1.028eV.

^b If the MCSCF and MRCI are expanded to include the 3d orbital as active, the EA is increased by 0.017eV.

^c Reference 6.