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# Size-inconsistency effects in molecular properties for states with valence-Rydberg mixing: The low-lying $\pi \rightarrow \pi^*$ states of ethylene and butadiene

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*Ab initio* results for the low-lying  ${}^1B_{1u}$  states of ethylene are used to discuss size-inconsistency effects on calculated molecular properties for states where valence-Rydberg mixing is important. Results for the expectation value of  $x^2$ ,  $x$  being the coordinate perpendicular to the plane of the molecule, are presented from quasidegenerate variational perturbation theory and multireference configuration-interaction calculations. These results are compared with values from previous studies. It is argued that size inconsistency in configuration-interaction studies can have a significant effect on estimated molecular properties. Calculations on several low-lying states of butadiene are also reported where similar size-inconsistency effects are found.

## I. INTRODUCTION

The low-lying  $\pi \rightarrow \pi^*$  states of unsaturated hydrocarbons have presented a formidable challenge to *ab initio* quantum chemistry. The low ionization potentials of these molecules lead to low-lying Rydberg states that can interact with nearby valence excited states, and the extent of mixing is highly sensitive to the theoretical method used. Ethylene is an excellent example of this problem.

Early *ab initio* calculations on the low-lying  $\pi \rightarrow \pi^*$  states of ethylene produced excitation energies far too large when compared with experiment if conventional valence-type basis sets were used.<sup>1</sup> Calculations by Dunning, Hunt, and Goddard<sup>2</sup> showed that an optimum energy was obtained for the lowest  ${}^1B_{1u}$  state if a truly Rydberg-like basis function was included in the calculation. This wave function led to an oscillator strength too small relative to the integrated experimental value. Correlated wave functions for ethylene were obtained by a variety of groups,<sup>3-6</sup> and it was shown that inclusion of correlation leads to a significant contraction in the spatial extent of the  ${}^1B_{1u}$  state. However, while the estimated vertical excitation energy seems to have converged to approximately 8.1–8.3 eV,<sup>3,5,6</sup> the spatial extent of this state is still in question. McMurchie and Davidson used a configuration-interaction (CI) scheme that included all double excitations involving at least one of the  $\pi$  electrons and obtained an expectation value for  $x^2$  of 17.3 a.u.<sup>4</sup> Inclusion of a subset of all sigma double excitations led to a small increase in  $\langle x^2 \rangle$ .<sup>4</sup> Buenker *et al.*<sup>3(b)</sup> used a multireference CI scheme based on iterative natural orbitals in a relatively large one-electron basis and obtained a value for  $\langle x^2 \rangle$  of 20 a.u. Earlier calculations by Brooks and Schaefer<sup>5</sup> also based on singles and doubles CI in natural orbital bases obtained an  $\langle x^2 \rangle$  of 26 a.u. The basis set used in Ref. 3(b) includes an extra  $d$  function on each carbon relative to that used in Ref. 5. More recently, multiconfiguration self-consistent field (MCSCF) calculations on the ethylene  ${}^1B_{1u}$  state have produced values of  $\langle x^2 \rangle$  on the order of 24 a.u. with the basis set and geometry of Brooks and Schaefer,<sup>5</sup> still lower values were expected if the geometry of Ref. 3 was used.

We have developed a multireference-based perturbation theory suitable for consideration of molecular excited states.<sup>7,8</sup> A method for calculating molecular properties based on these correlated wave functions was also presented.<sup>8</sup> This quasidegenerate variational perturbation theory (QDVPT) is more nearly size consistent than singles and doubles configuration interaction. In testing this method on the ethylene  ${}^1B_{1u}$  state using the basis set and geometry of Ref. 5, we obtained a value for  $\langle x^2 \rangle$  of 23 a.u., whereas a singles and doubles CI using the same two reference functions yielded a value near 28 a.u. It was suggested that this difference might be due to the size inconsistency of the singles and doubles CI (SDCI). However, the QDVPT properties were calculated as derivatives with respect to field strength using an approximation (equivalent to the assumption that the reference state is not altered with application of the perturbing field) that could not be ruled out at the time as the source of the discrepancy between QDVPT and SDCI.

In the present article several results are presented which seek to address the differences found between the QDVPT and SDCI values of  $\langle x^2 \rangle$ . First, the adequacy of the approximation used to evaluate QDVPT properties for these states is addressed. Finite-field calculations are performed to estimate  $\langle x^2 \rangle$ , where the reference space is allowed to readjust with application of the field. It is found that the spatial extent of the  ${}^1B_{1u}$  state decreases, not increases relative to the approximate QDVPT property. Second, after demonstrating that increase of the reference space size minimizes the effects of this approximation in a truncated configuration basis, expanded reference space QDVPT and SDCI results are presented for the ethylene  ${}^1B_{1u}$  states. It is seen that the two methods converge to a value of  $\langle x^2 \rangle$  near 22 a.u. Configuration-interaction and QDVPT results are then presented for several low-lying states of *trans*-1,3 butadiene. Similar size-inconsistency effects are observed for the lowest singlet  $\pi \rightarrow \pi^*$  states of butadiene. Finally, these results and their implications for other systems are discussed. Since the primary aim of the present article is to illustrate size-inconsistency effects in mixed valence-Rydberg states, a basis similar to that of Ref. 5 is used for ease of comparison.

## II. METHODS

All calculations reported below were performed using the MELDF suite of electronic structure codes.<sup>9</sup> Self-consistent-field wave functions were obtained from restricted Hartree–Fock calculations. The *s* components of all *d* functions were deleted at the SCF step. The molecular orbitals (MO's) used for the  ${}^1B_{1u}$  states of butadiene were the average natural orbitals<sup>10,11</sup> of the two lowest states in a preliminary SDCI calculation based on the Hartree–Fock MO's for the lowest singlet  $\pi \rightarrow \pi^*$  state in each case. In this preliminary SDCI all single excitations and all double excitations involving the  $\pi^*$  electron were included. It has been found that this set of average natural orbitals yields a compact and balanced description of the two lowest  $\pi \rightarrow \pi^*$  states in ethylene and the three shortest polyenes.<sup>7,11–13</sup>

The atomic basis sets used were similar to those of Ref. 5. The Dunning–Huzinaga<sup>14</sup> (9*s*,5*p*/4*s*,2*p*) set for carbon and the scaled ( $\alpha = 1.2$ ) (4*s*/2*s*) set for H were augmented with polarization functions (C: *d* = 0.75; H: *p* = 1.00) and two diffuse *p<sub>x</sub>* functions were added to each carbon (exponents equal 0.034 and 0.012). The geometry of Ref. 5, taken from Kuchitsu,<sup>15</sup> was used as well. The molecule is assumed to lie in the *yz* plane. The basis set used for butadiene was identical to that used for ethylene. The geometry used for butadiene was taken from Haugen and Traetteberg,<sup>16</sup> with the assumption that all C=C–H bond angles are equivalent.

A perturbation-theory (PT) selection and extrapolation scheme was used for the larger reference space calculations.<sup>7,17</sup> Where this is done the percentage of the second-order perturbation-theory energy accounted for by the configurations included in the variational portion of the calculation is reported (percentage of perturbation theory energy kept: percent PTK). Extrapolated energies are denoted by  $E^{\text{ex}}$ . The quasidegenerate variational perturbation-theory results are based on the method reported in Ref. 8. The reference functions are treated as a quasidegenerate space, and the correlation contributions from those configurations outside the reference space are treated in an approximately size-consistent manner.<sup>8</sup> Unlike SDCI, QDVPT results are sensitive to the choice of zeroth-order wave function even when PT selection is not performed. The results presented below for the singlet and triplet  $\pi \rightarrow \pi^*$  states are obtained from an iterative scheme where the present zeroth-order wave function is defined based on the coefficients of the reference space configurations for the full wave function from the previous iteration. For ethylene this procedure was repeated until the coefficients in the full wave function agreed with the zeroth-order coefficients of that iteration to at least  $\approx 0.0001$  for the two-reference results. This gives at least three place accuracy in the final properties. For the expanded reference results on ethylene convergence of the coefficients defining the zeroth-order wave function was obtained to  $\approx 0.001$  and to  $\approx 0.04$  for butadiene.

CI properties were calculated as expectation values of the given property. QDVPT properties were calculated as energy derivatives with respect to addition of the property to the Hamiltonian. The MO's used in all calculations were the zero-field MO's for each state. In Ref. 8 it was shown for QDVPT that if the reference wave function is defined as an

eigenfunction of the zeroth-order Hamiltonian for all values of the field the expression for the energy derivative can be used to define a one-particle density matrix analogous to that obtained for a CI wave function [Eqs. (47) and (50) of Ref. 8]. A similar result holds if the coefficients defining the reference state are fixed for all values of the field. This is because all other coefficients in QDVPT are variationally determined and a modified Hellmann–Feynman theorem<sup>18</sup> thus exists for QDVPT.<sup>8</sup> When the reference wave function is not obtained as an eigenfunction of the zeroth-order Hamiltonian and the reference space coefficients are allowed to vary with the applied field, an additional term of the form

$$-2|C_c\rangle\langle C_p|H|\partial C_p/\partial\lambda\rangle \quad (1)$$

enters the expression for the property.  $C_c$  is the vector of coefficients for the configurations outside the reference space in the zero-field QDVPT wave function,  $C_p$  is the vector defining the zeroth-order wave function, and  $\lambda$  is the field strength. This term was neglected in Ref. 8, thus properties were calculated assuming that the reference space was frozen as the field was applied. These are referred to below as “frozen-reference” results. In order to assess this approximation finite-field calculations were performed on ethylene where  $\pm 0.0001x^2$  or  $\pm 0.00001x^2$  was added to the Hamiltonian and the derivative with respect to  $\lambda$  used to estimate  $\langle x^2 \rangle$ . The zeroth-order space was iteratively defined as in the zero-field results. Note that in all cases (either when the density-matrix expression for the QDVPT property based on the energy derivative or the finite-field method is used) the MO's are the average natural orbitals for the zero-field case. Previous results by Bartlett *et al.*<sup>19</sup> have indicated that use of zero-field MO's in correlated finite-field calculations of molecular properties is an adequate approximation.

To test the effects of the term in Eq. (1) as the reference space size is increased, calculations were performed for ethylene using a truncated virtual space. In the untruncated set the irreducible representations  $a_g, b_{3u}, b_{2u}, b_{1u}, b_{3g}, b_{2g}, b_{1g}$ , and  $a_u$  had respectively 12, 6, 7, 12, 7, 6, 2, and 2, functions and in the truncated set the number of MO's in these symmetries were 8, 3, 4, 8, 4, 3, 1, and 1.

## III. RESULTS

In Table I results are presented from two-reference calculations on the ground state and the two lowest  ${}^1B_{1u}$  states of ethylene. The iterative procedure discussed in Sec. II was used to define the zeroth-order wave functions for the  ${}^1B_{1u}$  states and the MO's were the average natural orbitals for the lowest  ${}^1B_{1u}$  states from a previous small CI. The results for the  ${}^1A_g$  state are based upon the orbitals and two configurations from a two-configuration SCF for the  $\pi$  electrons. The zeroth-order wave function for the  ${}^1A_g$  state is obtained from diagonalizing the zeroth-order Hamiltonian.

The SDCI and QDVPT results for  $\langle x^2 \rangle$  for the  ${}^1A_g$  state are in excellent agreement. Note that the density-matrix formulation for the property is exactly equal to an energy derivative result for this state because the zeroth-order wave function is an eigenfunction of the zeroth-order Hamiltonian. For the  ${}^1B_{1u}$  states the present QDVPT “frozen-reference” result yields a smaller value of  $\langle x^2 \rangle$  for the  ${}^1B_{1u}$  state than does the two-reference singles and doubles CI. Conver-

TABLE I. Two-reference results for ethylene  ${}^1A_g$  and  ${}^1B_{1u}$  states.<sup>a</sup>

State	$E_0$	$E_{\text{QDVPT}}$	$\Delta E_{\text{QDVPT}}$	$\langle x^2 \rangle_{\text{QDVPT}}$	$E_{\text{CI}}$	$\Delta E_{\text{CI}}$	$\langle x^2 \rangle_{\text{CI}}$
1 ${}^1A_g$	-78.0782	-78.3616	...	11.7	-78.3356	...	11.7
1 ${}^1B_{1u}$	-77.7548	-78.0614	8.17	23.3	-78.0287	8.35	27.8
2 ${}^1B_{1u}$	-77.7328	-78.0206	9.28	70.6	-77.9911	9.37	59.2

<sup>a</sup>All quantities in atomic units except energy differences, which are in eV. The QDVPT properties for the  ${}^1B_{1u}$  states are based on "frozen-reference" results.

sely, the 2  ${}^1B_{1u}$  state is found to be significantly more diffuse in the QDVPT calculation than in the CI calculation. The frozen-reference QDVPT properties are based on a density matrix which neglects the contributions arising from Eq. (1) (see above and Ref. 8). It is possible that neglect of these terms is the reason for the discrepancy between QDVPT and CI. Note that calculation of the CI property as an energy derivative with fixed molecular orbitals would yield the same value as the expectation value calculation due to the Hellmann-Feynman theorem.<sup>18</sup> Thus, the difference cannot be attributed to what at first appears to be a different method of calculating the property.

To examine the effects of neglect of the contributions arising from Eq. (1), finite-field calculations were performed for QDVPT. The results of these calculations are shown in Table II. It is seen that inclusion of the terms of Eq. (1) (performed here by straightforward calculation of the energy derivative) actually decreases the spatial extent of the lowest  ${}^1B_{1u}$  state while it increases  $\langle x^2 \rangle$  for the second state in QDVPT. Thus, it is clear that other factors must be responsible for the differences between the SDCI and QDVPT properties for these states.

Results are presented in Table III from extended reference space calculations for the lowest  ${}^1B_{1u}$  states of ethylene where the virtual space has been truncated. The purpose of these calculations was (1) to compare the frozen-reference properties and the finite-field results where the full energy derivative with respect to field strength is calculated, and (2) to compare SDCI and QDVPT results based on a larger reference space with and without PT selection. It is seen that even with just a modest increase in reference space size the two methods for QDVPT property evaluation yield quite close results. This being the case the QDVPT properties for expanded reference spaces will be calculated using the density-matrix formulation, that is, neglecting terms arising from Eq. (1). It is also seen that the selected and unselected

CI results are within about 1 a.u. of one another; this holds true for selected and unselected QDVPT results as well.

In Table IV extended reference space calculations are presented for both QDVPT and SDCI. It is seen that as the reference space is increased the two methods give similar values for  $\langle x^2 \rangle$  which are in the range of 21–22 a.u. In these calculations perturbation theory was used to select a subset of the single and double excitations to be treated variationally. Based on comparison of the property results of Table III with those of Table IV, and also based on past experience with perturbation-theory selection effects on properties, PT selection is not expected to introduce significant errors.

In Table V results are shown from perturbation-theory selected calculations on the 1  ${}^1A_g$  and the lowest  ${}^1B_u$  and  ${}^3B_u$  states of *trans*-1,3 butadiene. Similar results are obtained to those obtained for ethylene. In particular, the ground-state description is similar for SDCI and QDVPT, but the lowest  ${}^1B_u$  state is significantly less diffuse in the QDVPT descriptions than in the CI results. SDCI and QDVPT results for the lowest triplet state are presented, and it is seen that they are essentially identical, as they were for the ground state. This state has been shown previously to be a pure valence state,<sup>20</sup> thus one expects it to behave in a similar fashion to the ground state. For the two-reference results on the 1  ${}^1B_u$  state PT selection was performed using  $\Psi_0$  and its orthogonal complement in the zeroth-order space, since PT selection on only one zeroth-order root can result in a bias when significant state mixing occurs.<sup>11</sup> It should be noted that percent PTK is rather low in the calculation of the two-reference 1  ${}^1B_u$  state, and the values of  $\langle x^2 \rangle$  would probably change if a larger variational calculation was performed. However, the calculations still point to effects similar to those observed in ethylene: a state of mixed valence-Rydberg character is more diffuse in the SDCI description than in the QDVPT. An expanded reference calculation on the  ${}^1B_u$  state was performed where the dominant configurations for both the first and second states of  ${}^1B_u$  symmetry were included. It is seen that expansion of the reference space has little effect on the CI results and leads to a small expansion of the  ${}^1B_u$  state in QDVPT. The QDVPT result is still significantly smaller than the CI result however. In these calculations it is crucial to perform perturbation-theory selection on the two lowest  ${}^1B_u$  states, since selection on only the lowest root led to a contraction in  $\langle x^2 \rangle$  that was not seen when the less-biased two-root selection was employed.

In Table VI two different size-consistency corrections are applied to the singles and doubles CI results of Table V and excitation energies are presented for QDVPT, SDCI,

TABLE II. Two-reference results for finite-field calculations of  $\langle x^2 \rangle$  for ethylene  ${}^1B_{1u}$  states.<sup>a</sup>

State	$E_0$	$E_{\text{QDVPT}}$	$\mu$	$\langle x^2 \rangle_{\text{FF}}$
1 ${}^1B_{1u}$	-77.755 29	-78.061 634	+ 0.000 01	
1 ${}^1B_{1u}$	-77.754 27	-78.061 245	- 0.000 01	19.4
2 ${}^1B_{1u}$	-77.733 21	-78.021 318	+ 0.000 01	
2 ${}^1B_{1u}$	-77.773 24	-78.019 837	- 0.000 01	74.1

<sup>a</sup>All quantities in atomic units.

TABLE III. QDVPT and SDCI results for  $\langle x^2 \rangle$  for ethylene  ${}^1B_{1u}$  states using a truncated virtual space.<sup>a</sup>

Zero Field						
State	$E_0$	$E_{\text{QDVPT}}$	$E_{\text{CI}}$	$\langle x^2 \rangle_{\text{QDVPT}}$	$\langle x^2 \rangle_{\text{CI}}$	
1 ${}^1B_{1u}$	-77.792 39	-77.988 61	-77.972 60	21.9	22.7	
2 ${}^1B_{1u}$	-77.758 63	-77.947 75	-77.933 15	65.3	64.8	
Zero-field PT selected						
State	$E_0$	Percent PTK	$E_{\text{QDVPT}}^{\text{ex}}$	$E_{\text{CI}}^{\text{ex}}$	$\langle x^2 \rangle_{\text{QDVPT}}$	$\langle x^2 \rangle_{\text{CI}}$
1 ${}^1B_{1u}$	-77.792 39	99.5	-77.986 63	-77.971 21	22.7	23.4
2 ${}^1B_{1u}$	-77.758 63	99.6	-77.946 29	-77.932 03	64.4	64.0
Finite field						
State	$E_0$		$E_{\text{QDVPT}}$	$\mu$		$\langle x^2 \rangle_{\text{FF}}$
1 ${}^1B_{1u}$	-77.792 67		-77.988 824	+0.000 01		
1 ${}^1B_{1u}$	-77.792 12		-77.988 398	-0.000 01		21.3
2 ${}^1B_{1u}$	-77.759 24		-77.948 409	+0.000 01		
2 ${}^1B_{1u}$	-77.758 01		-77.947 095	-0.000 01		65.7

<sup>a</sup> All quantities in atomic units. The virtual space used is described in the text. The reference space is composed of 12 spin-adapted configurations. The PT selected results are based on the zeroth-order states used in the unselected zero-field calculations.  $E^{\text{ex}}$  denotes a perturbation theory extrapolated energy.

and both size-consistency corrected CI results. The energies marked  $E_Q^1$  are based on a simple multireference analogue<sup>3(b)</sup> of the Davidson correction.<sup>21</sup> In this case a term of the form  $(1 - \Sigma C_0^2)(E_{\text{CI}}^{\text{ex}} - E_0)$  is added to the perturbation-theory extrapolated energy, where  $\Sigma C_0^2$  is the sum of the squares of the coefficients in the reference space in the final wave function,  $E_{\text{CI}}^{\text{ex}}$  is the extrapolated singles and doubles CI energy, and  $E_0$  is the energy of the zeroth-order wave function. The energies marked  $E_Q^2$  have a term of the form  $[(1 - \Sigma C_0^2)/(2\Sigma C_0^2 - 1)](E_{\text{CI}}^{\text{ex}} - E_0)$  added to the perturbation-theory extrapolated energy yielding the energy expression<sup>22</sup>

$$E_Q^2 = E_0 + \frac{\Sigma C_0^2}{2\Sigma C_0^2 - 1}(E_{\text{CI}}^{\text{ex}} - E_0). \quad (2)$$

It is seen that  $E_Q^2$  reproduces the QDVPT total energies quite well, while  $E_Q^1$  is in significant disagreement. It is also seen that without a correction for size inconsistency (either via QDVPT or through a post-CI correction) significant errors are made in the estimate of excitation energies for butadiene for the  ${}^1B_{1u}$  states.

#### IV. DISCUSSION

The present results indicate that within this basis set a reasonable estimate for the value of  $\langle x^2 \rangle$  for the 1  ${}^1B_{1u}$  state of ethylene is approximately 22 a.u. This falls in the middle of the range of previous estimates in this, or similar basis sets, and is close to the value found by Buenker *et al.*<sup>3</sup> It is also seen that when a minimum reference space is used to describe the two states of interest SDCI results tend to be too large for the lowest state. However, as the reference space is enlarged SDCI and QDVPT yield essentially the same result.

There are several reasons to suspect that the small reference SDCI's tend to overestimate the value of  $\langle x^2 \rangle$  due to size-inconsistency effects. First, in calculations in the above average natural-orbital basis where only single and double excitations involving the  $\pi^*$  electron were included, a value of  $\langle x^2 \rangle$  of 17.9 a.u. was obtained. Expansion of the CI to include all single and double excitations from the two-reference configurations for the  ${}^1B_{1u}$  states leads to a larger 1  ${}^1B_{1u}$  state, even though all the configurations contained in the smaller calculation are contained in the larger one.

Second, multireference SDCI (MRSDCI) is known to become more nearly size consistent as the reference space is

TABLE IV. Extended reference space results in the full virtual space for  $\langle x^2 \rangle$  for ethylene  ${}^1B_{1u}$  states.<sup>a</sup>

State	No. of refs.	$E_0$	Percent PTK	$E_{\text{QDVPT}}^{\text{ex}}$	$\langle x^2 \rangle_{\text{QDVPT}}$	$E_{\text{CI}}^{\text{ex}}$	$\langle x^2 \rangle_{\text{CI}}$
1 ${}^1B_{1u}$	12	-77.791 99	99.9	-78.064 52	20.5	-78.0391	21.4
1 ${}^1B_{1u}$	52	-77.810 88	99.1	-78.061 38	21.2	-78.0407	22.0
2 ${}^1B_{1u}$	12	-77.759 57	99.9	-78.021 92	68.7	-77.9984	66.6
2 ${}^1B_{1u}$	52	-77.780 55	99.2	-78.019 14	67.2	-78.0004	65.6

<sup>a</sup> All quantities in atomic units except where noted. No. of refs. is the number of spin-adapted configurations in the zeroth-order wave function. Percent PTK is the percentage of the second-order Rayleigh-Schrödinger energy accounted for by the configurations treated variationally.  $E^{\text{ex}}$  indicates a perturbation-theory extrapolated energy.

TABLE V. Results for several low-lying states of butadiene.<sup>a</sup>

State	No. of refs.	$E_0$	Percent PTK	$E_{\text{QDVPT}}^{\text{ex}}$	$\langle x^2 \rangle_{\text{QDVPT}}$	$E_{\text{CI}}^{\text{ex}}$	$\langle x^2 \rangle_{\text{CI}}$
$1^1A_g$	1	-154.949 64	91.6	-155.5311	21.3	-155.4378	22.0
$1^1A_g$	10	-154.993 89	90.4	-155.5309	22.0	-155.4577	22.0
$1^3B_u$	1	-154.838 29	90.3	-155.4136	21.4	-155.3151	21.9
$1^3B_u$	21	-154.868 18	85.7	-155.3964	21.9	-155.3270	21.4
$1^1B_u^b$	2	-154.711 13	78.9	-155.3151	45.8	-155.2102	52.9
$1^1B_u^b$	24	-154.738 47	84.4	-155.2962	48.1	-155.2141	52.8
$2^1B_u^b$	24	-154.702 85	84.7	-155.2716	52.8	-155.1850	48.0

<sup>a</sup> All quantities in atomic units. Definitions of quantities as in Table IV.

<sup>b</sup> Results based on PT selection on two zeroth-order roots.

expanded, and as that is done for the  $1^1B_{1u}$  states the size of the  $1^1B_{1u}$  state decreases. The results of Buenker and Peyerimhoff<sup>3</sup> were based on expanded reference spaces, and they obtained values of  $\langle x^2 \rangle$  similar to those obtained here for the larger CI's. In addition, MCSCF results for the  $1^1B_{1u}$  state in a basis comparable to that used here produce smaller values of  $\langle x^2 \rangle$  than the two-reference SDCI result.<sup>6</sup>

Third, the two-reference QDVPT result for the  $1^1B_{1u}$  state is much more contracted than the two-reference MRSDCI result. This is important to note, since otherwise one could suggest that the overestimate of the size of  $\langle x^2 \rangle$  was due to lack of possible important configurations in the two-reference SDCI. The two-reference QDVPT calculation uses the same reference space and includes the same correlating configurations as the two-reference SDCI, and yields a contracted  $1^1B_{1u}$  state. It appears that while the reference space and correlating configurations included in the two-reference case are sufficient to produce a value of  $\langle x^2 \rangle$  near that of the larger results, this does not occur in the SDCI. However, for the  $1^1A_g$  and  $1^3B_{1u}$  states, the QDVPT and MRSDCI results are in essentially exact agreement for one- and two-reference calculations.<sup>8</sup>

Thus, it would appear that the difference between SDCI and QDVPT for  $\langle x^2 \rangle$  in the  $1^1B_{1u}$  states when small reference spaces are used is due primarily to size inconsistency in the CI results. It is interesting to examine how size inconsistency might affect the valence-Rydberg mixing that accounts for the value of  $\langle x^2 \rangle$  obtained for the  $1^1B_{1u}$  states. At the single-configuration level the Rydberg configuration is lower in energy than the valence configuration for the  $\pi \rightarrow \pi^*$  state. One can show this by examining the SCF result for the  $1^1B_{1u}$  state, which is essentially Rydberg-like. The mixing

between these two zeroth-order states is thus brought on only when correlation is included. Using a Löwdin partitioning of the Hamiltonian, one can rewrite the CI equations as an effective Hamiltonian in the two-configuration space for the two lowest  $1^1B_{1u}$  states. The matrix elements are now those of the two configurations "dressed" by their interactions with the correlating configurations. At this level the energy spacing between the dressed valence and dressed Rydberg states will be less than at the single-configuration level, since the correlation energy is larger for the valence level. However, in a truncated CI size-inconsistency effects will diminish the contribution to the correlation energy of individual single and double excitations. Moreover, these correlation contributions will be diminished as more configurations are included. Therefore, for a fixed reference space SDCI one will bias towards a Rydberg-like state as configurations are included which contribute essentially equal energy lowerings to both zeroth-order states (such as  $\sigma\sigma'$  excitations). This could be part of the reason that the CI1 and CI2 results of McMurchie and Davidson<sup>4</sup> yield smaller values of  $\langle x^2 \rangle$  than the larger two-reference SDCI results above, or those of Brooks and Schaefer.<sup>5</sup> This brings up the interesting possibility that one could actually hurt the general description of the state of interest by correlating core electrons, for example, due to size-inconsistency effects. One expects that size inconsistency will only manifest itself in an increase in the spatial extent of a state when there are close-lying Rydberg levels. Thus, one obtains much closer agreement between SDCI and QDVPT for the  $1^1A_g$  and  $1^3B_{1u}$  states of ethylene.

It is interesting to note that the QDVPT results are also sensitive to expansion of the reference space, but for different

TABLE VI. Comparison of QDVPT and size-consistency corrected CI results.<sup>a</sup>

State	No. of refs.	$\Delta E_{\text{CI}}^{\text{ex}}$	$E_Q^1$	$\Delta E_Q^1$	$E_Q^2$	$\Delta E_Q^2$	$\Delta E_{\text{QDVPT}}^{\text{ex}}$
$1^1A_g$	10	...	-155.5125	...	-155.5294	...	...
$1^3B_u$	21	3.56	-155.3792	3.63	-155.3946	3.67	3.66
$1^1B_u$	24	6.63	-155.2730	6.51	-155.2923	6.45	6.39
$2^1B_u$	24	7.42	-155.2465	7.24	-155.2675	7.13	7.06

<sup>a</sup> Total energies in atomic units, energy differences in eV. Total energies for  $E_{\text{CI}}^{\text{ex}}$  and  $E_{\text{QDVPT}}^{\text{ex}}$  are in Table V.

reasons than the CI results. QDVPT is a perturbative approach, and the description it offers is generally improved as the description of the zeroth-order state is improved. Thus, QDVPT changes as  $\Psi_0$  is improved but converges quickly to a value near 21 a.u.

Butadiene is an example of a larger system where size-inconsistency effects are expected to be important, and the results of Table V suggest that they lead to even larger differences than those seen in ethylene. The ground state and first triplet state both have about the same spatial extent in SDCI or QDVPT. In a two-reference function calculation the  $1^1B_u$  state is smaller in QDVPT than in SDCI by approximately 8 a.u. Note that the QDVPT and CI calculations are based on the same set of PT selected configurations and the same zeroth-order wave function. As the reference space is increased in size the QDVPT  $\langle x^2 \rangle$  becomes somewhat larger, but still does not approach the CI value, which does not change with reference space size at this level of treatment. One expects some adjustment of the value of  $\langle x^2 \rangle$  as the reference space size is further increased or the size of the variational calculation is expanded, but based on the ethylene results it is expected that the QDVPT results are more accurate than the SDCI results.

It should be noted that even with the discrepancies observed between the QDVPT and SDCI descriptions of the mixed valence-Rydberg states, the qualitative conclusions drawn from previous CI results still hold: (1) the  $\pi \rightarrow \pi^*$  states of ethylene and butadiene are significantly more diffuse than normal valence states, and (2) the vertical excitation energies to the singlet  $\pi \rightarrow \pi^*$  states are found to be larger than those estimated from the intensity maxima in the corresponding absorption spectra.

In calculating excitation energies it is seen that it is crucial to account for size inconsistency to obtain accurate results, and that the  $E_Q^2$  values are somewhat closer to the QDVPT results than the  $E_Q^1$  excitation energies. In addition, the  $E_Q^2$  total energies were in quite good agreement with QDVPT. These are improved relative to the  $E_Q^1$  energies because the expression for  $E_Q^2$  takes account of renormalization of  $\Sigma C_0^2$  as the expansion size and correlation energy increase. This suggests that SDCI with post-CI correction for size inconsistency may be more accurate than one might have expected for large systems. Further testing needs to be done on this point.

The results on size-inconsistency effects on molecular properties have implications for calculations on excited-state potential-energy surfaces near curve crossings for strongly dissimilar states. A common example would be a crossing between an ion-pair state and a Rydberg state, such as is found in  $Cl_2$ .<sup>23</sup> In this case one has two states that when dressed by their interactions with excited determinants are nearly degenerate, but which have quite different correlation energies. The above results suggest that size inconsistency may manifest itself in other properties than merely the total energies. For example, the positions of avoided crossings could be shifted by artificially raising the energy of the ion-pair state relative to the Rydberg level if SDCI is used. Another example would be in the calculation of transition moments as a function of internuclear distance in the regions of

curve crossings. If the mixing of the two states is improperly described by a size-inconsistent method, one can obtain matrix elements where the contribution of the Rydberg-like configuration has been overemphasized.

## V. CONCLUSIONS

Results of multireference SDCI and quasidegenerate variational perturbation-theory calculations are presented on the two lowest  $1^1B_{1u}$  states of ethylene and several low-lying states of butadiene. It is seen that the two methods converge to a value of about 22 a.u. for  $\langle x^2 \rangle$  for the  $1^1B_{1u}$  state,  $x$  being the coordinate perpendicular to the plane of the molecule. Results of calculations are also presented that test the adequacy of an approximate method for property evaluation for QDVPT wave functions when the reference wave function is not an eigenfunction of the zeroth-order Hamiltonian. On the basis of the SDCI and QDVPT results it is argued that truncated CI tends to overestimate the size of the  $1^1B_{1u}$  state of ethylene and the  $1^1B_u$  state of butadiene due to size-inconsistency effects. It was also found that an approximate size-consistency correction to SDCI is capable of producing total energies in quite good agreement with QDVPT for butadiene. The implications of size inconsistency for properties other than the total energy are discussed.

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