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Orbital Correlation Effects: The Independent Pair-Potential Approximation with Application to the Ground State and First Ionized State of Boron Hydride

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A new method is proposed for calculating correlation effects in atomic and molecular systems. The basis of the method is the formulation of a set of partial configuration expansions which yield directly variational orbital correlation corrections which are appropriately summed in order to obtain an estimate of the total correlation energy. This method is applied to the ground state of boron hydride and its cation at the equilibrium distance of BH. The results of the method are compared in detail with independent electron pair results and second order CI results. It is further shown that multiple substitutions are approximately accounted for in this method and the extent to which they are included is compared with other approximations. Finally, three methods of increasing accuracy, aimed at reducing the necessary computational effort, are given for determining the vertical ionization potential. The most economical method yields an IP of 9.70 eV or 0.03 eV less than the experimental IP. Completion of the basis is estimated to improve this value to 9.77 eV.

Key words: Boron hydride – Correlation energy – Ionization potential – Orbital correlation

1. Introduction

The last 15 years has seen a good deal of progress in the evaluation of electron correlation corrected wavefunctions and properties of atoms and molecules. One of the central contributing factors to this progress has been the idea of decoupling the N-electron system into smaller subsystems by neglecting a portion of the coupling elements arising in the exact Schrödinger equation, and at the same time truncating the many-body expansion at a low order while implicitly including higher order effects [1].

Decoupling has its origins in nuclear theory [2] and in the early sixties the concept was taken over by a number of workers in atomic and molecular physics and adapted to the non-infinite systems met in this area. Sinanoğlu [3], working on the basis of a cluster development of the exact wavefunction, developed methods for determining pair corrections to the Hartree-Fock (HF) wavefunction. Nesbet [4], on the other hand, attempting to stay as close as possible to the familiar Configuration Interaction (CI) method, developed a scheme, which in principle can be extended to obtain the exact energy and wavefunction, for calculating pair correlation corrections by performing a number of partial CI calculations.

These methods when considered together have as their central assumption that next to the independent particle approximation, the main correction comes from electron-pair interactions which can be treated independently [5]. The term Independent Electron Pair Approximation (IEPA) [6] has therefore been applied to all these calculational procedures.

The IEPA has been applied succesfully to atoms [7–11] and a number of small molecules [12–15]. At the same time there is some evidence [15–17] that the quality of the approximation differs from system to system. It can further be expected that it deteriorates with delocalization, since in that case the structure of a given pair will be strongly modified by interactions with other electrons.

When the IEPA fails, is it necessary or desirable to retain the decoupling concept? Within Nesbet's scheme it is possible to include higher order subgroups [4] in the calculation, but the increase in computation which is then required obviates much of the advantage gained by introducing decoupling. In a recent paper Meyer [18] has developed a method for carrying out second order CI calculations with a considerable reduction in computational effort. This has been achieved by partially relaxing the orthogonality requirement between the orbitals. At the same time he proposed a coupled electron pair approach, which allows for approximately including the effects of higher order substitutions in the second order CI wavefunction. Nevertheless, no matter how efficient the computation, decoupling with its concomitant reduction in matrix size and the number of matrix elements which have to be calculated, will require less computational effort then the corresponding coupled calculation. Because of this, decoupling will remain an attractive alternative, provided that the approximations which are made are not to severe.

In order to improve the IEPA it is necessary to make less severe decoupling assumptions. We do this by including a class of coupling elements in the formulation and computation, which are neglected in the IEPA. This change leads quite naturally to the idea of *independent orbital correlation corrections* instead of independent pair correlation corrections as will be discussed below.

Giving up part of the decoupling of the IEPA yields a concomitant increase in computing requirements, but because the coupling between disjoint pairs is still excluded, the new method still provides a saving over variational second order CI calculations as was discussed in a previous note [19]. In the first section, the method is formulated and the proposed approximation is discussed. In Section 3 the scheme is applied to BH and compared with the IEPA and second order CI. The details of the approximation are also discussed. Finally, in the third part it is shown that the approximation proposed here is well suited for calculating the energy changes associated with one-electron processes. As an example the first ionization potential of BH is determined.

2. Formulation of the IPPA Method

2.1. Introductory Remarks

Consider an N-electron system with hamiltonian $\mathscr{H}$ and wavefunction of the form

$$\Psi = \Phi_0 + X \tag{1}$$

where

$$\langle \Phi_0 | \Phi_0 \rangle = \langle \Phi_0 | \Psi \rangle = 1\,, \tag{2}$$

$$\langle \Phi_0 | X \rangle = 0\,, \tag{3}$$

and

$$\Phi_0 = \sum_K C_K \Delta_K\,. \tag{4}$$

The Δ_K are determinants constructed from a complete set of orthonormal spin-orbitals and the C_K are expansion parameters. The function Ψ may be approximate or exact.

The total energy calculated from the wavefunction defined in Eq. (1) can be written in the form

$$E = E_0 + \varepsilon \tag{5}$$

where E_0 is the reference state energy given by

$$E_0 = \langle \Phi_0 | \mathscr{H} | \Phi_0 \rangle \tag{6}$$

and ε is the energy shift [3]

$$\varepsilon = (2\langle \Phi_0 | \mathscr{H} | X \rangle + \langle X | \mathscr{H} - E_0 | X \rangle)/(1 + \langle X | X \rangle)\,. \tag{7}$$

When Ψ is exact wavefunction Eq. (7) can be replaced by

$$\varepsilon = \langle \Phi_0 | \mathscr{H} | X \rangle \tag{8}$$

and now the crux of the problem resides in knowing the function X. In case X is an approximation, solution of the Schrödinger Equation in the configuration space defining Ψ still leads to an energy shift of the form of Eq. (8) [9], so that it can be used in approximate calculations as well. One example of this is the IEPA where a contribution of the form of Eq. (8) is determined for each independent electron pair.

2.2. The Exact Orbital Correlation Method

In the present formulation, orbital correlation corrections will be considered rather than independent pair or higher independent subgroup corrections [4]. We start with the second order orbital corrections by considering trial wavefunctions of the form

$$\Psi_i^{(2)} = \Phi_0 + \sum_j \sum_a C_j^a \Phi_j^a + \sum_{j(\neq i)} \sum_{ab} C_{ij}^{ab} \Phi_{ij}^{ab}\,. \tag{9}$$

The $\Phi_{ij\ldots}^{ab\ldots}$ are excited configurations where the occupied spin-orbitals $\phi_i, \phi_j, \ldots$ have been replaced by unoccupied spin-orbitals $\phi_a, \phi_b, \ldots$ [20], and the $C_{ij\ldots}^{ab\ldots}$ are variation parameters. The first sum in Eq. (9) is the total first order correction obtained by including all singly substituted configurations. The second sum represents the second order correction for orbital ϕ_i. It is constructed by including all double substitutions obtained by replacing occupied spin-orbitals ϕ_i and ϕ_j by unoccupied spin-orbitals ϕ_a and ϕ_b and letting the index j take on all values $[1, N]$ excluding i.

The matrix form of the Schrödinger equation for this trial wavefunction is

$$\begin{aligned} E_i^{(2)} &= E_0 + \sum_{j,a} \langle \Phi_0 | \mathcal{H} | \Phi_j^a \rangle C_j^a + \sum_{j(\neq i)} \sum_{ab} \langle \Phi_0 | \mathcal{H} | \Phi_{ij}^{ab} \rangle C_{ij}^{ab} \\ &= E_0 + \sum_j \bar{\varepsilon}_j + \sum_{j(\neq i)} \bar{\varepsilon}_{ij} \end{aligned} \tag{10a}$$

where the $\bar{\varepsilon}_{ij}$ are the pair correlation energies, and

$$\begin{aligned} (E_i^{(2)} - \langle \Phi_{ij}^{ab} | \mathcal{H} | \Phi_{ij}^{ab} \rangle) C_{ij}^{ab} &= \langle \Phi_0 | \mathcal{H} | \Phi_{ij}^{ab} \rangle + \sum_{k,c} \langle \Phi_{ij}^{ab} | \mathcal{H} | \Phi_k^c \rangle C_k^c \\ &+ \sum_{cd(\neq ab)} \langle \Phi_{ij}^{ab} | \mathcal{H} | \Phi_{ij}^{cd} \rangle C_{ij}^{cd} + \sum_{k(\neq i,j)} \sum_{cd} \langle \Phi_{ij}^{ab} | \mathcal{H} | \Phi_{ik}^{cd} \rangle C_{ik}^{cd} . \end{aligned} \tag{10b}$$

Solution of this equation yields the expectation value $E_i^{(2)}$ from which we define the net second order orbital correlation energy by

$$\varepsilon_i^{(2)} = E_i^{(2)} - E_0 - \varepsilon^{(1)} \tag{11}$$

where $\varepsilon^{(1)}$ is the net first order correlation energy to be defined below.

Trial wavefunctions are constructed for all N occupied orbitals, and by solving Eqs. (10) for each trial wavefunction, N second order orbital correlation energies are obtained. The total net second order correlation energy is given by

$$\varepsilon^{(2)} = \tfrac{1}{2} \sum_i \varepsilon_i^{(2)} \tag{12}$$

where the multiplicative factor $\frac{1}{2}$ corrects for the fact that substitutions from a given pair occur in two orbital wavefunctions (OW). Thus the sum of the net orbital correlation energies includes every pair energy contribution twice.

We can now extend the method to higher orders: For the third order the orbital trial wavefunctions have the form

$$\Psi_i^{(3)} = \Phi_0 + \sum_{j,a} C_j^a \Phi_j^a + \sum_{jk} \sum_{ab} C_{jk}^{ab} \Phi_{jk}^{ab} + \sum_{j,k(\neq i)} \sum_{abc} C_{ijk}^{abc} \Phi_{ijk}^{abc} \tag{13}$$

where the last term gives the third order correction for an electron occupying ϕ_i with the $N-1$ remaining electrons. The first and second sums in Eq. (13) are the complete first and second order corrections, respectively. Solution of the Schrödinger equation in the configuration space defining $\Psi_i^{(3)}$ yields the expectation value $E_i^{(3)}$ for orbital ϕ_i and the net third order orbital correction

$$\varepsilon_i^{(3)} = E_i^{(3)} - E_0 - \varepsilon^{(1)} - \varepsilon^{(2)} . \tag{14}$$

In the third order there are again N net orbital correlation corrections. The net total third order correlation energy is

$$\varepsilon^{(3)} = (1/3) \sum_i \varepsilon_i^{(3)} \tag{15}$$

where the factor 1/3 corrects for the fact that substitutions from a given triple ijk appear in three third order trial wavefunctions.

This procedure can now be carried out to any order one chooses, and at every order N orbital wavefunctions are constructed and N net orbital correlation corrections are obtained. The total n'th order correction is

$$\varepsilon^{(n)} = (1/n) \sum_i \varepsilon_i^{(n)} . \tag{16}$$

Continuing through order N[1] we will have obtained N net correlation corrections, and it is easily verified that the exact energy shift is then given by

$$\varepsilon = \sum_n^N \varepsilon^{(n)} = \sum_n \sum_i (1/n)\, \varepsilon_i^{(n)}\,. \tag{17}$$

2.3. Proposed Approximation

The result of performing the entire procedure is, of course, equivalent to solving the N-electron Schrödinger equation exactly, which means that the procedure is only useful if it can be truncated at a very early stage [4]. Indeed, our proposal is to truncate the scheme at the second order and to replace the exact Eq. (17) with the approximation

$$\varepsilon \approx \varepsilon^{(1)} + \tfrac{1}{2} \sum_i \varepsilon_i^{(2)} \tag{18}$$

so that the entire calculation reduces to a series of N second order variational calculations.

In contrast to the IEPA where the effective potential contains an interaction term for the pair under consideration [21], the effective potential for the approximation proposed here will contain the pair interactions between an electron occupying orbital ϕ_i and the $N-1$ remaining electrons in the system. These interactions can be considered as the orbital potential corrections to the average potential experienced by the electron in the field of $N-1$ Hartree-Fock electrons. The terminology Independent Pair-Potential Approximation (IPPA) seems appropriate for this scheme and will be used throughout the remaining parts of this paper.

When the reference state orbitals do not satisfy the Hartree-Fock equations, comparison of the IEPA and IPPA energy matrices[2] shows that the IEPA matrix contains only those first order coupling elements obtained from single substitutions of the occupied pair under consideration. On the other hand, the IPPA matrix contains all first order coupling elements. This fact makes the method used for evaluating $\varepsilon^{(1)}$ somewhat arbitrary. One can calculate it from a first order Nesbet-Bethe-Goldstone (NBG) type calculation [4] or directly from the trial wavefunction

$$\Psi^{(1)} = \Phi_0 + \sum_{i,a} C_i^a \Phi_i^a \tag{19a}$$

with

$$\varepsilon^{(1)} = E^{(1)} - E_0 = \sum_i \bar{\varepsilon}_i \tag{19b}$$

where $E^{(1)}$ is the expectation value of $\Psi^{(1)}$. Whichever method is used, the exact energy shift calculated from Eq. (17) is unaffected, but the approximate energy shift calculated from Eq. (18) does change slightly depending on which method is used. Which procedure is to be preferred will be seen later.

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[1] The procedure has to be done N times only in a formal sense for the Nth order, since $E_i^{(N)}$ is the exact energy for every i, i.e., $\Psi_i^{(N)}$ is the exact wavefunction.

[2] The IEPA energy matrix is obtained from Eqs. (10a) and (10b) by omitting all first order terms except those for orbitals i and j and omitting the last sum in Eq. (10b).

3. Application to BH

3.1. Details of the Calculation

We have chosen BH as a test case for investigating the numerical valididty of the proposed scheme. Calculations using the σ and π basis functions from the basis proposed by Bender and Davidson [22] have been carried out. By using a truncated basis it was possible to perform both incomplete and complete CI calculations and to compare the approximation being proposed here with the IEPA and with second order CI. All calculations were carried out at an internuclear separation of 2.336 bohr and the basis yielded an SCF energy of -25.12963 a.u. as compared with Cade and Huo's [23] result of -25.13137 a.u.

In terms of the spin-orbit formulation presented in the previous section, six calculations would in principle have to be performed for BH with a ground state configuration $1\sigma 1\bar{\sigma} 2\sigma 2\bar{\sigma} 3\sigma 3\bar{\sigma}$. For example, the $\Psi^{(2)}_{1\sigma}$ trial wavefunction would contain all the singly substituted configurations and doubly substituted configurations from occupied pairs $1\sigma 1\bar{\sigma}$, $1\sigma 2\sigma$, $1\sigma 2\bar{\sigma}$, $1\sigma 3\sigma$, and $1\sigma 3\bar{\sigma}$. The calculations reported here were, however, carried out using programs written in terms of spin-adapted configurations [22], and the trial wavefunctions are restricted to be eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$. Therefore the singly and doubly substituted configurations are identified in terms of space-orbitals only, and the orbital correlation energies and pair correlation energies discussed below are the space-orbital results. In addition, for the remainder of this section, contributions from singly substituted configurations are neglected.

For BH then, three IPPA trial wavefunctions have to be constructed, namely $\Psi_{1\sigma}$, $\Psi_{2\sigma}$, and $\Psi_{3\sigma}$ where the superscript (2) has been dropped. Table 1 gives schematically the structure of each type of OW and the corresponding pair energy contributions. $\Psi_{1\sigma}$, for example, includes contributions from the pairs $1\sigma^2$, $1\sigma 2\sigma$, and $1\sigma 3\sigma$. Table 1 further shows that the correlation energy recovered by each OW is just the sum of the contributions from the included pairs, i.e., the (space)-orbital correlation energies (OCE).

Equation (12), which is valid for the spin-orbit formulation, has to be modified slightly in the space-orbit formulation because now the intra-shell pairs appear in only one of the orbital wavefunctions while the inter-shell pairs appear in two

Table 1. IPPA orbital wavefunction (OW) structure and derived energy quantities for BH

OW	Pairs included in OW $1\sigma^2$	$1\sigma 2\sigma$	$2\sigma^2$	$1\sigma 3\sigma$	$2\sigma 3\sigma$	$3\sigma^2$	OCE[a,b]
1σ	×	×		×			$\Sigma\bar{\varepsilon}_{i,1\sigma}$
2σ		×	×		×		$\Sigma\bar{\varepsilon}_{i,2\sigma}$
3σ				×	×	×	$\Sigma\bar{\varepsilon}_{i,3\sigma}$
Multiplication factor for pair contr. to $\varepsilon^{(2)}$	1	$\frac{1}{2}$	1	$\frac{1}{2}$	$\frac{1}{2}$	1	$\varepsilon^{(2)}$

[a] If OW's include single substitutions, the OCE's will also include a correction for them. See Table 7.

[b] The $\bar{\varepsilon}_{ij}$ are defined in Eq. (10a).

orbital wavefunctions [24]. From Table 1 it is seen that the entires in the columns are summed and the result is multiplied by one or one-half as indicated. Finally all the pair contributions are summed to obtain the total second order correlation correction.

The orbital basis used for constructing the trial wavefunctions was obtained by combining the canonical SCF orbitals with a set of excited orbitals derived from a single natural orbital iteration [25] beyond the SCF level. Throughout the iteration the occupied orbitals were frozen so that any contributions from singly substituted configurations would remain negligible, and their exclusion would not affect the main results of these calculations.

Since the total number of configurations which can be constructed for the IPPA trial wavefunctions can still be quite large, it is of interest to investigate the convergence properties of wavefunctions expanded with only a partial set of the possible configurations. Without requiring that the orbital basis is optimal in the iterative natural orbital sense [22, 25], calculations have been carried out using a truncated set of configurations for each occupied pair (Incomplete Configuration Interaction, ICI) and a complete set of configurations (Complete Configuration Interaction, CCI). The trial wavefunctions used in the ICI calculations were constructed from 776 of the 1519 possible space configurations which can be formed from the basis. The configurations were selected with the help of second order perturbation theory [22], and only those configurations with an energy contribution greater then 10^{-4} a.u. were retained.

3.2. *Energy Results for* BH

With these two types of configuration expansions, IEPA, IPPA and second order CI calculations were performed. The global results are reported in Table 2. It is seen that for all three approximations the ICI expansion recovers about 85% of the CCI correlation energy. Table 2 also lists results from some other calcu-

Table 2. Correlation energy results for IEPA, IPPA and 2*d*-order CI calculations on BH. $R = 2.336$ bohr

	ICI		CCI		
Approximation	Correlation energy (a.u.)	% below 2*d*-order CI	Correlation energy (a.u.)	% below 2*d*-order CI	%[a]
IEPA	−0.11775	3.3	−0.13910	6.2	84.7
IPPA	−0.11726	2.9	−0.13792	5.3	84.9
2*d*-order CI	−0.11393		−0.13103		86.9

Results from other calculations (in a.u.)

	IEPA
B and D[b]	−0.1484 (−0.1332)
V and N[c]	−0.07783
G[d]	−0.13692

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[a] Percent CCI correlation energy recovered by ICI.

[b] Ref. [22]. The result in parentheses is the correlation energy from the 2*d*-order CI calculation.

[c] Ref. [14].

[d] Ref. [13].

lations. Comparison of our second order results with Bender and Davidson's [22] should be made on the basis of our ICI calculation which indicates that their result is more converged then that of the present calculation. Comparison of our IEPA results with those of Gélus *et al.* [13] suggests that the quality of our basis set is about the same as theirs.

The principal result exhibited in Table 2 is the difference in the energy shifts, which demonstrates the effects of the approximations being made in the three approaches.

Both the IEPA and the IPPA make essentially two different approximations [18], namely

a) Neglect of certain types of coupling terms between different pairs.

b) Approximate inclusion of the effect of unlinked clusters through partial neglect of normalization.

The difference in the correlation energy recovered by complete second order CI wavefunctions and the experimental correlation energy is due to the neglect of higher order terms which are implicitly included in the IEPA and IPPA through the second approximation above. This implies that any approximation which includes the effects of higher order substitutions will have to yield an additional energy lowering of 5–10% [26] of the correlation energy recovered by a second order CI calculation. Previous calculations have shown, however, that IEPA results can still be quite far from the experimental results [15–17], probably because both approximations (a) and (b) are too extreme. On the other hand, the fact that the CCI energy shifts for the IPPA and the IEPA calculations reported in Table 2 are 5.3% and 6.2% greater then the second order CCI energy shift, respectively, indicates that the IPPA still accounts for the most important higher order interactions while at the same time correcting, at least partially, for the defects of the IEPA.

Tables 3 and 4 tabulate the results from the IPPA calculations. Comparing the results listed in Table 3 with those given in Table 4, shows that the overall character of the ICI calculation is the same as the CCI calculation. In particular, the ordering of the OCE's is the same in both cases. The percentage orbital correlation energy recovered by the ICI trial wavefunctions is also given in Table 3. From these it is seen that the extent of convergence of the three OW's is by no means the same and exhibits a large variation around the 85% total correlation energy recovered. For the 3σ OCE this is at least partially due to the presence of the $1\sigma^2 2\sigma^2 1\pi^2$ configuration which is nearly degenerate with the reference state.

Table 3. IPPA-ICI pair correlation energy analysis of BH (energies in atomic units)

OW	$-\bar{\varepsilon}_{ij}$							
	$1\sigma^2$	$1\sigma 2\sigma$	$2\sigma^2$	$1\sigma 3\sigma$	$2\sigma 3\sigma$	$3\sigma^2$	$-\varepsilon_i^{(2)}$	%[a]
1σ	0.03591	0.00303		0.00345			0.04239	98
2σ		0.00297	0.02502		0.02294		0.05093	83
3σ				0.00337	0.02307	0.02691	0.05335	77
	0.03591	0.00300	0.02502	0.00341	0.02301	0.02691	0.11726	85

[a] Percent CCI correlation energy recovered by ICI.

Table 4. IPPA-CCI pair correlation energy analysis of BH (energies in atomic units)

				$-\bar{\varepsilon}_{ij}$				
OW	$1\sigma^2$	$1\sigma 2\sigma$	$2\sigma^2$	$1\sigma 3\sigma$	$2\sigma 3\sigma$	$3\sigma^2$	$-\varepsilon_i^{(2)}$	R[a]
1σ	0.03623	0.00322		0.00361			0.04306	0.18
2σ		0.00309	0.02907		0.02891		0.06107	1.1
3σ				0.00342	0.02862	0.03718	0.06922	0.86
	0.03623	0.00316	0.02907	0.00352	0.02876	0.03718	0.13792	

[a] Ratio of intershell orbital correlation energy to intrashell orbital correlation energy.

The mixing coefficient for this configuration is rather unstable, varying from about 0.1 in the ICI calculations to about 0.2 in the CCI calculations. This instability is probably due to the particular form of the orbitals used here, and is also the source of the large difference in the unlinked cluster effect between the ICI and CCI calculations. The results obtained here for the ICI calculations indicate that some care must be taken in insuring a balanced convergence when carrying out a number of partial CI calculations. The ICI calculations are currently being reinvestigated with improved basis sets, and initial results show that convergence is entirely satisfactory when care is taken in obtaining optimized natural orbitals [22]. These investigations will be described elsewhere [27].

From Table 4 it is further seen that the main effect in the 1σ OW is due to the contribution from the $1\sigma^2$ pair while the $1\sigma 2\sigma$ and $1\sigma 3\sigma$ intershell pair energies are only about 10% as large. On the other hand, the valence shell shows no such preference for a particular pair. This effect is clearly demonstrated in the last column of Table 4 where the ratio of the intershell to the intrashell correlation energy is tabulated for each OW. The results show that the $1\sigma^2$ pair is essentially independent, while the four valence shell electrons exhibit strong interactions. These conclusions are in agreement with the results obtained from previous calculations [13, 22, 28].

Table 5 lists the pair energies for all three approximations. These results show that the energy contributions from the $1\sigma^2$, $1\sigma 2\sigma$, and $1\sigma 3\sigma$ pairs are not very sensitive to the type of approximation used, indicating that many-body effects make only a small or negligible contribution to these pairs. The difference between the valence shell pairs, however, demonstrates the effect of the approxi-

Table 5. Pair correlation energy analysis of IEPA, IPPA, and 2*d*-order CCI calculations for BH

pair	IEPA $-\bar{\varepsilon}_{ij}$	IPPA from Table 4	2*d*-order CI $-\bar{\varepsilon}_{ij}$
$1\sigma^2$	0.03625	0.03623	0.03613
$1\sigma 2\sigma$	0.00324	0.00316	0.00308
$2\sigma^2$	0.02896	0.02907	0.02716
$1\sigma 3\sigma$	0.00364	0.00352	0.00341
$2\sigma 3\sigma$	0.02885	0.02876	0.02781
$3\sigma^2$	0.03816	0.03718	0.03343

mations being made and shows that here the many-body interactions have an important influence on the results. The ratio of inter- to intrashell correlation energy for each orbital in the IEPA and second order CI calculation is essentially the same as the ratios given in Table 4.

It is not possible to compare the IEPA results obtained here directly with those of Bender and Davidson [22] or with the results of Gélus *et al.* [13] because the three calculations are based on three different types of occupied orbitals [29]. Bender and Davidson [22] used occupied natural orbitals while Gélus *et al.* [13] used localized orbitals [30]. Here the canonical SCF orbitals are used. The effect on the OCE's of a unitary transformation over the occupied orbitals has not yet been determined. It is, however, possible to calculate approximate OCE's from the IEPA results. Comparison of approximate OCE's computed from the IEPA pair energies given in Table 5 with the OCE's computed from Gélus *et al.* [13] results indicates that the OCE's are considerably less sensitive to unitary transformations than the pair energies.

3.3. Analysis of the IPPA *Method*

The energy matrix, given by Eqs. (10), shows that the IPPA neglects only the disjoint coupling elements between different pairs, while the IEPA neglects both semi-disjoint and disjoint coupling elements^2. From the second order CCI calculation reported in Table 2 it is possible to determine these elements and make some assessment of the effect of their neglect in the IEPA and the IPPA. The energy contributions obtained from the coupling elements between different pairs are defined by

$$(ij|kl) = \sum_{ab}\sum_{cd} \langle \Phi_{ij}^{ab} | \mathscr{H} | \Phi_{kl}^{cd} \rangle C_{ij}^{ab} C_{kl}^{cd} \tag{20}$$

and are given in Table 6. The sum of the semi-disjoint contributions and the sum of the disjoint contributions are also listed for each pair. Inspection of Table 6 shows that the $(2\sigma^2|2\sigma 3\sigma)$, $(3\sigma^2|2\sigma 3\sigma)$, and $(2\sigma^2|3\sigma^2)$ coupling elements make the largest contributions, and that the two semi-disjoint coupling elements are negative while the disjoint element is positive.

Table 6. Semi-disjoint and disjoint coupling elements from 2*d*-order CCI on BH[a]. (Atomic units)

pair	$1\sigma 2\sigma$	$2\sigma^2$	$1\sigma 3\sigma$	$2\sigma 3\sigma$	$3\sigma^2$	semi-disjoint[b]	disjoint[c]
$1\sigma^2$	2.66 −6	1.42 −5	2.88 −5	4.83 −6	1.33 −5	3.15 −5	3.23 −5
$1\sigma 2\sigma$		1.37 −4	8.53 −6	6.07 −5	7.11 −6	2.09 −4	7.11 −6
$2\sigma^2$			−2.15 −6	−1.72 −3	1.56 −3	−1.58 −3	1.57 −3
$1\sigma 3\sigma$				7.68 −5	2.05 −4	3.19 −4	−2.15 −6
$2\sigma 3\sigma$					−1.91 −3	−3.49 −3	4.83 −6
$3\sigma^2$						−1.71 −3	1.58 −3

[a] Energies reported are defined in Eq. (20).

[b] Sum of all contributions of the type $(ij|ik)$ over $k \neq i, j$ for pair ij.

[c] Sum of all contributions of the type $(ij|kl)$ over $k, l \neq i, j$ for pair ij.

Referring now to the total semi-disjoint and disjoint contributions, it is seen that the largest are one order of magnitude smaller then the respective pair energies to which they contribute. In addition, the overall effect of the semi-disjoint coupling terms is energy lowering while the effect of the disjoint elements is energy raising. A more detailed examination shows that for the $1\sigma^2$ pair both types of coupling elements are very small and probably have little effect on the structure of this pair in the IPPA and second order CI calculation. For the remaining pairs the semi-disjoint contributions are significant while only the disjoint elements belonging to the $2\sigma^2$ and $3\sigma^2$ pairs are large enough to make non-negligible constributions. For the last two pairs the effect of the semi-disjoint coupling elements is almost entirely cancelled by the contribution from the disjoint coupling elements. The effect of neglecting coupling elements is in general difficult to estimate *a priori.* Nevertheless, the magnitude of the semi-disjoint and disjoint elements listed in Table 6 are not very large, and on the whole the latter are smaller then the former.

It is also of interest to indicate how the unlinked cluster effect is included in the IPPA formulation. In order to do this we follow, formally, a recent derivation given by Meyer [18] for including unlinked cluster effects in second order CI calculations. Consider the second order CI wavefunction and extend the configuration space to include all higher order effects, Φ_K, possible within the basis. One has

$$\Psi = \Phi_0 + \sum_{ij}\sum_{ab} C_{ij}^{ab}\Phi_{ij}^{ab} + \sum_{K} C_K\Phi_K \,. \tag{21}$$

The Schrödinger equation is given by

$$E = E_0 + \sum_{ij} \bar{\varepsilon}_{ij} \tag{22a}$$

and

$$(E - \langle\Phi_{ij}^{ab}|\mathscr{H}|\Phi_{ij}^{ab}\rangle)\, C_{ij}^{ab} = \langle\Phi_{ij}^{ab}|\mathscr{H}|\Psi - \Phi_{ij}^{ab}C_{ij}^{ab}\rangle \,. \tag{22b}$$

We now introduce the approximation

$$\sum_{K} \langle\Phi_{ij}^{ab}|\mathscr{H}|\Phi_K\rangle\, C_K \approx C_{ij}^{ab} \sum_{k,l(\neq i)} \bar{\varepsilon}_{kl} \tag{23}$$

which implies the assumption that unlinked clusters are the main source of higher order effects. Equation (10b) is obtained from Eq. (22b) by removing all the disjoint coupling elements from the latter and inserting Eq. (23) into Eq. (22b), which with rearrangement yields the IPPA energy denominator.

Equation (23) gives the extent to which multiple substitutions are implicitly included in the IPPA in the form of unlinked clusters. The change in the energy denominator of Eq. (22b) obtained by inserting Eq. (23) into it is

$$\varepsilon \rightarrow \bar{\varepsilon}_{ij} + \sum_{k(\neq i,j)} \bar{\varepsilon}_{ik}$$

and is intermediate between the energy shift leading to the IEPA [18, 30]

$$\varepsilon \rightarrow \bar{\varepsilon}_{ij}$$

and the energy shift obtained by Kelly [32] from perturbation theory, i.e.,

$$\varepsilon \rightarrow \bar{\varepsilon}_{ij} + \sum_{k(\neq i,j)} \bar{\varepsilon}_{ik} + \bar{\varepsilon}_{kj} \,.$$

The absence of the sum $\Sigma \bar{\varepsilon}_{kj}$ in the IPPA energy denominator is due to the orbital formulation of the method. Comparison of these three energy denominators shows that the extent to which the IPPA accounts for multiple substitutions is just intermediate between the IEPA [18, 31] and Kelly's perturbation theory [32].

It is also possible to introduce couplings into the energy denominator of the IPPA equations accounting for the other occupied orbitals in the system. The effectiveness of such procedures will be considered elsewhere.

It should finally be mentioned that the IPPA is currently being applied to some other systems which include occupied π orbitals. Results obtained so far indicate no major revisions in the conclusions reached here concerning the general applicability of the IPPA.

4. Calculation of Energy Changes in One-Electron Processes

4.1. Formulation of Methods for Calculating Vertical Ionization Potentials

The fact that the IPPA yields orbital correlation corrections suggests that it would be possible to apply it with an appreciable reduction in computational effort to estimating the energy changes associated with one-electron changes from the ground state configuration. Energy shifts arising from excitation, ionization or negative-ion formation come under consideration as typical one-electron changes.

In order to test this conjecture we calculate the first vertical ionization potential (IP) of BH, i.e.,

$$\mathrm{IP} = E(\mathrm{BH}^+) - E(\mathrm{BH}) \tag{24}$$

where BH^+ is in the configuration $1\sigma^2 2\sigma^2 3\sigma$. The calculations are to be carried out under the following guiding conditions:

a) Avoid an additional integral transformation by using the frozen orbitals obtained from the initial state.

b) Obtain the changes in correlation energy, in so far as possible, directly from the OW of the orbital under consideration.

Within this framework the reference state of BH^+ is constructed from the canonical HF-SCF orbitals of BH which is then augmented by all possible singly substituted configurations. These first order corrections account for relaxation of the occupied orbitals to the approximate Hartree-Fock wavefunction of the final state and for polarization [3].

Beyond these corrections a number of second order corrections have to be accounted for [18]:

a) Additional types of double substitutions which can be formed in the final state due to enlargement of the correlation space. In BH^+ these are the semi-internal [9] correlations.

b) Change in external correlation [9] due to the removal of an electron from the frozen initial state wavefunction.

c) Change in external correlation arising from the deformation of all orbital pairs involving the orbital under consideration, i.e., the $1\sigma 3\sigma$ and $2\sigma 3\sigma$ pairs.

d) Change in external correlation due to deformation of remaining pairs.

The first two effects should make the largest contribution while (c) and (d) are expected to be small [3, 18]. By including two, three or all of these effects, three methods for calculating the IP are formulated as follows:

1. For BH^+ construct the trial wavefunction

$$\Psi = \Phi_0 + \sum_{i,a} C_i^a \Phi_i^a + \sum_{i,j(\neq 3\sigma)} \sum_a C_{ij}^{3\sigma,a} \Phi_{ij}^{3\sigma,a} \tag{25}$$

where the third term in this wavefunction gives the semi-internal correlations. The energy results from the 3σ OW of BH are used for the initial state. From the initial and final state calculations the change in reference state energy, ε_0, the change in energy due to singly substituted configurations, ε_s, and the energy contribution, ε_{si}, from the semi-internally substituted configurations are calculated. The change in external correlation is computed from the pair energies obtained from the 3σ OW of BH, namely

$$\varepsilon_{\mathrm{corr}} = -\left(\tfrac{1}{2}\bar{\varepsilon}_{1\sigma 3\sigma} + \tfrac{1}{2}\bar{\varepsilon}_{2\sigma 3\sigma} + \bar{\varepsilon}_{3\sigma^2}\right). \tag{26}$$

The ionization potential may then be obtained from the sum

$$\mathrm{IP} = \varepsilon_0 + \varepsilon_s + \varepsilon_{si} + \varepsilon_{\mathrm{corr}} \tag{27}$$

and does not include any correlation changes due to the deformation of orbitals.

2. The 3σ OW of BH^+, modified to include the semi-internal substitutions, is determined. The IP is now given directly by

$$\mathrm{IP} = E_{3\sigma+si}(BH^+) - E_{3\sigma}(BH). \tag{28}$$

Alternatively one can determine ε_{si} from the wavefunction of Eq. (25) and determine the remaining changes from the unmodified 3σ OW of BH^+. The difference in the calculated IP between these two procedures is probably not greater then 0.01 eV. In both cases the change in external correlation is determined from

$$\varepsilon_{\mathrm{corr}} = \varepsilon_{3\sigma}^{(2)}(BH^+) - \varepsilon_{3\sigma}^{(2)}(BH). \tag{29}$$

Thus, in this approximation the correlation energy changes arising from deformations in the pairs $1\sigma 3\sigma$ and $2\sigma 3\sigma$ are also included.

3. Carry out a complete IPPA calculation for BH^+ and determine the IP from

$$\mathrm{IP} = \varepsilon_0 + \varepsilon_s + \varepsilon_{\mathrm{corr}} \tag{30}$$

where

$$\varepsilon_{\mathrm{corr}} = \varepsilon^{(2)}(BH^+) - \varepsilon^{(2)}(BH). \tag{31}$$

$\varepsilon_{\mathrm{corr}}$ includes the energy effects of the semi-internal correlations and all energy changes due to deformations of excited orbitals in the final state.

4.2. *Orbital Wavefunctions and* IPPA *Correlation Energy of* BH^+

In order to carry out the calculations described in Section 2.1, the orbital wavefunctions and orbital correlation energies of BH^+ are needed. The first order trial wavefunction has the form given by Eq. (19a) and yields an energy of -24.82389 a.u. for BH^+ ($R = 2.336$ b.) and an IP of 8.32 eV as compared with -24.82064 ($R = 2.296$ b.) and 8.45 eV obtained by Cade and Huo [23] for the

Table 7. IPPA-CCI pair energy analysis for BH^+, $R = 2.336$. (Atomic units)

OW	$\varepsilon^{(1)} - \Sigma\bar{\varepsilon}_i$[a]	$-\bar{\varepsilon}_{ij}$					$-\varepsilon_i^{(2)}$
		$1\sigma^2$	$1\sigma 2\sigma$	$2\sigma^2$	$1\sigma 3\sigma$	$2\sigma 3\sigma$	
1σ	−0.00187	0.03641	0.00363		0.00207		0.04024
2σ	−0.00129		0.00356	0.03155		0.01393	0.04775
3σ	−0.00059				0.00206	0.01398	0.01545
	−0.00187	0.03641	0.00359	0.03155	0.00207	0.01395	0.08570
$\varepsilon^{(1)}$							0.04225
$\varepsilon^{(1)} + \varepsilon^{(2)}$							0.12795

[a] $\varepsilon^{(1)}$ is the net first order correction obtained from $\Psi^{(1)}$. $\Sigma\bar{\varepsilon}_i$ is the first order contribution obtained from the OW's.

SCF energy and IP, respectively. The difference between the two results is primarily due to the inclusion of polarization effects not present in Cade and Huo's [23] RHF results.

The estimate of $\varepsilon^{(1)}$ obtained from Eqs. (19) is preferable to evaluating it from a series of first order NBG calculations because the coupling elements are not necessarily negligible when the singly excited configurations contribute strongly. The value of $\varepsilon^{(1)}$ obtained from an NBG calculation is −0.04597 a.u. as compared with −0.04225 a.u. obtained from the variational calculation. In addition, it has been shown [33, 34] that first order unlinked cluster effects are small, so that their implicit inclusion following from first order NBG calculations may contribute an additional error.

The results of applying the IPPA to BH^+ are reported in Table 7. The first column gives the residual first order energy arising from the interaction between the singly and doubly substituted configurations. These effects are energy increasing. Comparison of the BH^+ results with the BH results given in Table 4 shows that the $1\sigma^2$ pair energy is essentially unchanged. The $2\sigma 3\sigma$ pair energy of BH^+ is nearly half that of BH, showing very little deformation due to ion formation. On the other hand, the BH^+ $1\sigma 3\sigma$ pair has deformed somewhat, and its contribution is larger than half the BH $1\sigma 3\sigma$ contribution. The large change in the $2\sigma^2$ pair energy is mainly due to the contribution from semi-internal substitutions. The bulk of the semi-internal correlation energy comes from substitutions $2\sigma^2 \rightarrow 3\sigma n\sigma$. Finally, the source of additional energy lowering of the BH^+ $1\sigma 2\sigma$ pair is due about one-third to the semi-internal correlations and two-thirds to deformation.

Combining the results of the first order wavefunction with the correlation energy reported in Table 7 yields a total energy of −24.90959 a.u. The experimental energy is −24.932 a.u. [23].

4.3. Vertical Ionization Potential

The IP's calculated by methods (1), (2), and (3) described in Section 3.1 are given in Table 8. Table 8 also lists the individual terms contributing to the IP

Table 8. Vertical ionization potential of BH, $R = 2.336$

Method	ε_0	ε_s	ε_{si}	$\varepsilon_{\text{corr}}$	IP (eV)
1	0.34800	-0.04195	-0.00281	0.05320	9.70
2	0.34800	-0.04166	-0.00281	0.05318	9.71
3	0.34800	-0.04225	—	0.05226	9.74
exp[a]					9.73 ± 0.01

[a] Adiabatic IP, see Ref. [23].

defined in Eq. (27) for methods (1) and (2) and in Eq. (30) for method (3). ε_s is obtained from Eq. (25), $\Psi_{3\sigma}(\mathrm{BH}^+)$ and Eqs. (19a, b) for methods (1), (2), and (3), respectively. ε_{si} is calculated from the wavefunction of Eq. (25) and used in both methods (1) and (2). The pair contributions to the semi-internal correlation are -0.00228, -0.00014 and -0.00039 a.u. for the $2\sigma^2$, $1\sigma 2\sigma$, and $1\sigma 3\sigma$ pairs, respectively.

The values of the calculated IP shows that deformation plays a very small role in the first vertical ionization potential of BH. Indeed, energy contributions from pairs including the 3σ orbital are only 0.01 eV, while the remaining deformations contribute only another 0.03 eV.

These results show that the bulk of the correlation effects contributing to the IP has been recovered. Method (1) can be expected to be most sensitive to the completeness of the basis set, but all calculations reported here suffer from the fact that the δ and φ orbitals are omitted. Comparison with Bender and Davidson's [22] results indicates that improvement of the basis will yield another 5% correlation energy. Applying this estimate to method (1) yields a vertical IP of 9.77 eV. Calculations with improved basis sets are currently under investigation. It is finally noted that the experimental IP given in Table 8 is the adiabatic IP, which is generally less then the vertical IP [35].

For the first ionization potential method (1), which requires the least computation, is expected to give a sufficiently accurate estimate of the IP to be useful in most cases. For higher IP's, and especially for inner-shell hole states, deformation can be considerable [18, 36], so that for these cases only methods (2) or (3) will suffice. Results for hole states will be reported elsewhere.

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