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Comparison of ab initio Effective Valence Shell Hamiltonian with Semiempirical Theories of Valence: Pairing Theorem

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The pairing properties of electronic structure are investigated from ab initioists' point of view. Numerical results of exact ab initio effective valence shell Hamiltonian are compared with simple semiempirical Hamiltonian calculations. In the oxygen atom case it was found that effective three-electron interaction terms break the similarity between electron-states and hole-states. With the *trans*-butadiene as an example the pairing theorem was studied. Even for alternant hydrocarbons, the deviation from the pairing was found to be enormous. The pairing theorem, which is usually stated for semiempirical Hamiltonians, is not valid when the exact effective Hamiltonian is considered. The present study indicates that comparisons between the pairing theorem of semiempirical methods and ab initio effective Hamiltonian give important information on the accuracy of semiempirical methods.

Introduction

In atomic spectra elements carbon and oxygen show a similar pattern, which is probably due to the nominally same electronic structure of the two elements. It is understood with the idea of electrons and holes in the similar 2p shell.[1] Carbon has two electrons in the 2p shell, while oxygen has two holes. The positive and negative ions of an alternant hydrocarbon also exhibit a very similar spectroscopic pattern.[2] This remarkable phenomenon is often explained using the so called pairing theorem in molecular orbital theory. But the pairing of two spectra does not hold exactly, as McLachlan[3] and Koutecký[4] showed that the pairing is valid only under certain approximations.

Any molecules or atoms have a finite number of electrons, but infinite number of single-electron orbitals are required to exactly describe the electronic structure of the systems. Therefore a number of electrons of a system can not be same as holes of any other systems. The concept of the equalness between a number of electrons and that of holes is valid only when a finite number of orbitals are considered. Usually valence orbitals are chosen for that purpose. For alternant hydrocarbons π orbitals are often considered as valence orbitals. So it is important to note that the pairing theorem holds only for an approximate Hamiltonian which spans on a finite valence space.

The well-known examples satisfying the pairing theorem are one-electron Hückel Hamiltonian[5] and Pariser-Parr-Pople (PPP) Hamiltonian[6-8] with zero differential overlap approximation. It indicates that the pairing properties of electronic structure are often stated in simple semiempirical theories. The pairing has not drawn any attentions from ab initioists who are always worried about extensive virtual orbitals.

Recently an ab initio effective valence shell Hamiltonian formalism which formally mimicks semiempirical Hamiltonians has been developed.[9-11] The full Hamiltonian is transformed to an effective one which spans on small valence space only, yet the transformation is performed exactly. The effective valence shell Hamiltonian is ab initio Hamitonian which conveniently generates useful effective integral values amongst valence orbitals. Therefore it is now possible to examine the validity of the pairing theorem of semiempirical Hamiltonians. The purpose of the present work is to understand when the pairing theorem is valid and furthermore to assess the accuracy of approximate semiempirical methods.

Extensive calculations of the effective valence shell Hamiltonian on various atoms[12,13] and *trans*-butadiene[14] have appeared in literature. Therefore in the present work we choose oxygen atom and *trans*-butadiene as our prototype system. The valence state of oxygen atom and its doubly positive ion, O^{2+}, are formally studied as an electron-hole model case. The pairing pro-

perties of *trans*-butadiene π orbitals are investigated in both semiempirical and ab initio ways.

The next section briefly describes the ab initio effective valence shell Hamiltonian formalism. The analyses on oxygen and butadiene systems are described in the following two sections. Our conclusion is summarized in the final section.

Effective Valence Shell Hamiltonian, $\mathscr{H}^v$

The full Hamiltonian is transformed to an effective one which acts within a small valence space. The valence space is composed of determinantal wavefunctions whose core orbitals are fully occupied and valence orbitals are partially occupied by valence electrons. The transformation can be performed in various ways. Freed and coworkers[9,11] adopted quasidegenerate many-body perturbation method to derive the ab initio effective valence shell Hamiltonian, $\mathscr{H}^v$.

The transformed $\mathscr{H}^v$ is written as

$$\mathscr{H}^v = E_c + \sum_i \mathscr{H}_i^v + \frac{1}{2} \sum_{i \neq j} \mathscr{H}_{ij}^v + \frac{1}{3!} \sum_{i \neq j \neq k} \mathscr{H}_{ijk}^v + \cdots \qquad (1)$$

where E_c is the core energy, $\mathscr{H}_i^v$, $\mathscr{H}_{ij}^v$, and $\mathscr{H}_{ijk}^v$ are one-, two- and three-electron operators, respectively. The indices *i, j*, and *k* indicate valence orbitals only. Unlike the full Hamiltonian, $\mathscr{H}^v$ must contain nonclassical many-electron operators ($\mathscr{H}_{ijk}^v$, etc.). The expansion in equation (1) should terminate at the N_v-electron operator where N_v is a number of valence electrons.

The properties of $\mathscr{H}^v$ are as follows: (1) $\mathscr{H}^v$ contains reference to only some prechosen set of valence shell orbitals. Nevertheless the eigenvalues of $\mathscr{H}^v$ are exactly identical with those of full Hamiltonian. (2) $\mathscr{H}^v$ formally mimicks model semiempirical Hamiltonians. This feature of $\mathscr{H}^v$ enables one to theoretically evaluate effective $\mathscr{H}^v$ integrals between valence orbitals which are empirically determined from experiments in semiempirical methods. (3) Unlike semiempirical Hamiltonians, many (three or up)-electron operators should exist in exact ab initio $\mathscr{H}^v$. (4) $\mathscr{H}^v$ uses the same valence orbitals for all valence states of the system including all different charge states. For example valence states energy levels of oxygen and its ion, O^{2+} can be determined with a same set of effective integrals, *i.e.*, matrix elements of $\mathscr{H}^v$.

The $\mathscr{H}^v$ method has been applied to various atomic and molecular systems. One of them is Lee *et al.*'s $\mathscr{H}^v$ calculation on *trans*-butadiene.[14] They utilized a large Gaussian basis set to obtain the results of which accuracy is comparable to that of other configuration interaction calculations. Various choices of π orbitals are tested and their implications are discussed. More importantly expectation values of effective operators, $\mathscr{H}^v$ etc., are computed. In the present work we take their $\mathscr{H}^v$ integral values as accurate ab initio theoretical values to understand the approximations implicitly embedded in the pairing theorem.

Electrons and Holes: Oxygen

The oxygen atom has the electronic configuration of $1s^2 2s^2 2p^4$. The O^{2+} ion has two less number of electrons so that its electronic configuration is $1s^2 2s^2 2p^2$. The three spatial 2p shell orbitals can contain maximum number of six electrons. It means that the oxygen ion, O^{2+} has two electrons in 2p shell while the

oxygen atom has two holes. Therefore spectra of the two systems are expected to be very similar, if not identical.

Theoretically exact ab initio effective Hamiltonian can be defined for the 2p shell space only. And evaluation of individual matrix elements of $\mathscr{H}^v$ is possible. Both of O and O^{2+} states are simultaneously determined with the same set of $\mathscr{H}^v$ matrix elements. The valence state energy expressions for the ^3P, ^1D and ^1S states of O and O^{2+} in terms of $\mathscr{H}^v$ matrix elements are derived Table 1 shows the excitation energy expressions from the ground ^3P state to the excited ^1D and ^1S states.

As shown in Table 1, the excitation energies of O^{2+} are expressed in terms of only one- and two-electron $\mathscr{H}^v$ integrals. It is because there are only two electrons in valence 2p shell. But the excitation energies of O have three- and four-electron $\mathscr{H}^v$ integrals. Sun *et al.*[13] showed in their various atomic calculations that three-electron $\mathscr{H}^v$ integrals are an order of magnitude smaller than two-electron $\mathscr{H}^v$ integrals. It implies that, though the two sets of excitation energies are not identical, they could be similar. This analysis also indicates that there can not exist a semiempirical Hamiltonian (which neglects three- and higher-electron terms) that describe both of O and O^{2+} valence states exactly. If the 2s orbital is included into valence space, there will be a little more flexibility in adjusting parameters in semiempirical way. However, still exact Hamiltonian can not be obtained in that way.

Pairing Theorem: *trans*-1,3-Butadiene

The pairing theorem notably from the Hückel method has been explained in a general fashion. McLachlan[3] showed that the theorem holds generally for certain approximate valence Hamiltonians even when multiconfigurations are considered. Koutecky[4] derived a general type of Hamiltonian which exhibits pairing properties. He also suggested various approximate self-consistent-field (SCF) type methods in which pairing properties are found. Here we note that the pairing theorem is valid for an approximate Hamiltonian, not for an exact Hamiltonian itself.

We choose a prototype alternant hydrocarbon, the *trans*-1, 3-butadiene as our example. For π type orbitals - one p orbital from each carbon — are chosen as valence orbitals for *trans*-butadiene π-Hamiltonian. The pairing theorem states that four molecular orbitals (MO) constructed from four carbon p orbitals are spread out in a certain fashion. The four MO's are two bonding orbitals, $\psi(1a_u)$ and $\psi(1b_g)$, and two antibonding

TABLE 1: Analytical Expressions for the Excitation Energies of O^{2+} and O

System	Excitation	Expressions in terms of integrals
O^{2+}	$^3P \rightarrow {}^1D$	$2\langle xy|yx\rangle$
	$^3P \rightarrow {}^1S$	$\langle xx|xx\rangle - \langle xy|xy\rangle + 3\langle xy|yx\rangle$
O^{2+}	$^3P \rightarrow {}^1D$	$2\langle xy|yx\rangle + 4\langle xyz|xzy\rangle + a$
	$^3P \rightarrow {}^1S$	$\langle xx|xx\rangle + 3\langle xy|yx\rangle - \langle xy|xy\rangle$
		$+2\langle xyy|xyy\rangle + 4\langle xyy|xzz\rangle$
		$-2\langle xyz|xyz\rangle + 2\langle xyz|xzy\rangle + a$

*. Four-electron terms are not listed. *. $\langle xyy|xzz\rangle = \langle p_x(1)p_y(2)p_y(3)|\mathscr{H}_{ijk}^v|p_x(1)p_z(2)p_z(3)\rangle$

orbitals, $\psi(2a_u)$ and $\psi(2b_g)$. The difference between the orbital energy, $\varepsilon(1a_u)$, of $\psi(1a_u)$ and that, $\varepsilon(1b_g)$, of $\psi(1b_g)$ is equal to the difference between $\varepsilon(2a_u)$ of $\psi(1b_g)$ and $\varepsilon(2b_g)$ of $\psi(2b_g)$. That is, in the simple Hückel method for *trans*-butadiene,

$$\varepsilon(1b_g) - \varepsilon(1a_u) = -\beta \qquad (2)$$

$$\varepsilon(2b_g) - \varepsilon(2a_u) = -\beta \qquad (3)$$

where β is resonance integral between neighboring two carbon p orbitals.

We designate $|1\rangle$ for the p orbital of terminal carbon, $|2\rangle$ for central carbon, $|3\rangle$ for the other central carbon and $|4\rangle$ for the other terminal carbon. Then the four MO's are

$$\psi(1a_u) = a_1|1\rangle + a_2|2\rangle + a_2|3\rangle + a_1|4\rangle$$
$$\psi(1b_g) = b_1|1\rangle + b_2|2\rangle - b_2|3\rangle - b_1|4\rangle$$
$$\psi(2a_u) = c_1|1\rangle - c_2|2\rangle - c_2|3\rangle + c_1|4\rangle$$
$$\psi(2b_g) = d_1|1\rangle - d_2|2\rangle + d_2|3\rangle - d_1|4\rangle \qquad (4)$$

All carbon p orbitals, $|1\rangle$, $|2\rangle$, $|3\rangle$ and $|4\rangle$ are ortho-normal to each other. If we define orbital energy, ε, as an expectation value of one-electron effective operator, $\mathscr{H}_i^v$, then

$$\varepsilon(1a_u) = \langle\psi(1a_u)|\mathscr{H}_i^v|\psi(1a_u)\rangle, \qquad (5)$$

etc. So the analytical expressions for equations (2) and (3) are

$$\varepsilon(1b_g) - \varepsilon(1a_u)$$
$$= 2(b_1{}^2 - a_1{}^2)\langle1|\mathscr{H}_i^v|1\rangle + 2(b_2{}^2 - a_2{}^2)\langle2|\mathscr{H}_i^v|2\rangle$$
$$+ 4(b_1b_2 - a_1a_2)\langle2|\mathscr{H}_i^v|1\rangle - 4(b_1b_2 + a_1a_2)\langle3|\mathscr{H}_i^v|1\rangle \qquad (6)$$
$$- 2(b_1{}^2 + a_1{}^2)\langle4|\mathscr{H}_i^v|1\rangle - 2(b_2{}^2 + a_2{}^2)\langle3|\mathscr{H}_i^v|2\rangle$$

$$\varepsilon(2b_g) - \varepsilon(2a_u)$$
$$= 2(d_1{}^2 - c_1{}^2)\langle1|\mathscr{H}_i^v|1\rangle + 2(d_2{}^2 - c_2{}^2)\langle2|\mathscr{H}_i^v|2\rangle$$
$$- 4(d_1d_2 - c_1c_2)\langle2|\mathscr{H}_i^v|1\rangle + 4(d_1d_2 + c_1c_2)\langle3|\mathscr{H}_i^v|1\rangle \qquad (7)$$
$$- 2(d_1{}^2 + c_1{}^2)\langle4|\mathscr{H}_i^v|1\rangle - 2(d_2{}^2 + c_2{}^2)\langle3|\mathscr{H}_i^v|2\rangle$$

The coefficients a_1 a_2, etc. can be obtained in various ways. Under the simple Hückel approximations,

$$a_2 = b_1 = c_1 = d_2 \qquad (8)$$

and

$$a_1 = b_2 = c_2 = d_1 \qquad (9)$$

If the coefficients are determined from SCF calculations, there are no evident relationships among the coefficients. Parr and Mulliken[17] determined the coefficients from SCF calculations with four atomic p orbitals (Slater type functions) on each carbon. The Hückel coefficients and SCF coefficients are listed in Table 2. Parr and Mulliken's atomic p orbitals are not orthogonalized. We orthogonalized the four carbon p orbitals and recalculated the corresponding coefficients which are also shown in Table 2.

If we have the effective $\mathscr{H}^v$ integrals, e.g., $\langle1|\mathscr{H}_i^v|1\rangle$, etc., we will be able to evaluate equations (6) and (7). Lee et al.[14] performed ab initio $\mathscr{H}^v$ calculations on *trans*-butadiene with a large extended basis set. In the $\mathscr{H}^v$ calculations correlated effective integrals among four valence π orbitals are computed. These efective $\mathscr{H}^v$ integrals correspond to so called parameters of semiempirical methods.[18-20] Performing valence configuration interaction calculations with effective $\mathscr{H}^v$ integrals, we can pro-

TABLE 2: Values of Coefficients in Four π MO's

Coefficients	Hückel	SCF[a]	SCF (orthogonal)[b]
a_1	0.3717	0.3540	0.4205
a_2	0.6015	0.4687	0.5686
b_1	0.6015	0.5081	0.5589
b_2	0.3717	0.4229	0.4332
c_1	0.6015	0.6452	0.5686
c_2	0.3717	0.4698	0.4205
d_1	0.3717	0.5343	0.4332
d_2	0.6015	0.7268	0.5589

[a]. Reference 17; [b]. Löwdin's symmetrical orthogonalization scheme was used.

duce all the valence state energies of the *trans*-butadiene. Consequently the Lee's $\mathscr{H}^v$ integrals are ab initio values of the integrals in equations of (6) and (7). The ab initio integrals are as follows; $\langle1|\mathscr{H}_i^v|1\rangle = -24.94$ eV, $\langle2|\mathscr{H}_i^v|2\rangle = -28.85$ eV, $\langle2|\mathscr{H}_i^v|1\rangle = -3.57$ eV, $\langle3|\mathscr{H}_i^v|1\rangle = -0.96$ eV, $\langle4|\mathscr{H}_i^v|1\rangle = -1.31$ eV, $\langle3|\mathscr{H}_i^v|2\rangle = -1.28$ eV. Here all carbon porbitals, e.g. $|1\rangle$, etc., are orthonormalized.

With the above $\mathscr{H}^v$ integrals and the Hückel coefficients in Table 2 we evaluate equations (6) and (7), which are

$$\varepsilon(1b_g) - \varepsilon(1a_u) = 6.06\text{eV} \qquad (10)$$

$$\varepsilon(2b_g) - \varepsilon(2a_u) = 2.62\text{eV} \qquad (11)$$

Using the orthogonalized SCF coefficients (third column in Table 2), we obtain

$$\varepsilon(1b_g) - \varepsilon(1a_u) = 5.55\text{eV} \qquad (12)$$

$$\varepsilon(2b_g) - \varepsilon(2a_u) = 3.50\text{eV} \qquad (13)$$

Equations (10) and (11), and equations (12) and (13) clearly show that $\varepsilon(1b_g) - \varepsilon(1a_u)$ is not equal to $\varepsilon(2b_g) - \varepsilon(2a_u)$ for both sets of coefficients. It means that the pairing theorem totally breaks down when the exact effective Hamiltonian of valence is considered. It might be a natural consequence of the exact ab initio effective Hamiltonian which must have more than one-electron terms.

We examine the Hückel method itself. In the Hückel Hamiltonian,

$$\langle1|\mathscr{H}_i^v|1\rangle = \langle2|\mathscr{H}_i^v|2\rangle = \alpha$$
$$\langle2|\mathscr{H}_i^v|1\rangle = \langle3|\mathscr{H}_i^v|2\rangle = \beta \qquad (14)$$
$$\langle3|\mathscr{H}_i^v|1\rangle = \langle4|\mathscr{H}_i^v|1\rangle = 0$$

where α is Coulomb integral and β is resonance integral. Using the relationships of (14) and the Hückel coefficients in Table 2, we readily obtain the equality of (2) and (3). Using the Hückel approximation of (14) and the orthogonalized SCF coefficients in Table 2, we again obtain the equality of (2) and (3). We find that the Hückel Hamiltonian satisfies the paring theorem since the approximate Hückel Hamiltonian is an effective one-electron Hamiltonian with approximations of (14).

Two spectra of *trans*-butadiene cation and anion are very similar, but it is readily expected that they are not identical. Since the cation has three electrons, the excitation energies of the cation involve one-, two-, and three-electron $\mathscr{H}^v$ terms. The anion excitation energies involve four- and five-electron terms besides one-, two- and three-electron $\mathscr{H}^v$ terms. As in the ex-