

Pair-correlation energies in sodium hydride with many-body perturbation theory*

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Many-body perturbation theory (MBPT) is applied to the electronic structure of the sodium hydride molecule using a basis set of Slater-type orbitals. Both a V^N and a V^{N-1} potential are considered for determining the virtual orbitals, but these are shown to give nearly equivalent results when all pairlike diagrams are summed through third order in the MBPT expansion using shifted denominators. A value of -0.2544 hartrees is obtained for the correlation energy, which is $\sim 59\%$ of the experimental value. A clear separation into intrashell and intershell correlation energy effects is observed.

I. INTRODUCTION

After Kelly's successful applications to atoms,¹ a great interest has developed in using the many-body perturbation theory (MBPT) of Brueckner and Goldstone^{2,3} to study various properties of molecules. One approach to this problem has been to use a one-center expansion with numerical orbitals.^{4,5} However, such procedures are impractical for multicenter molecular systems, and thus it is advantageous to use a conventional basis set consisting of a finite number of Slater- or Gaussian-type functions situated at each of the nuclear centers. Such an approach has been reported by Schulman and Kaufman⁶ for the H_2 molecule using a Gaussian set to calculate the second-order energy and first-order correlation corrections to some second-order properties. More recently, Kaldor⁷ has compared a finite basis study of the Be correlation energy with Kelly's⁸ results and obtained excellent agreement. Kaldor has also studied⁹ the excited states of H_2 using Schulman and Kaufman's Gaussian basis.

In the present work, we describe an application of MBPT to the ground state ($^1\Sigma^+$) correlation energy of sodium hydride, using the two-center Slater-orbital self-consistent-field (SCF) basis set of Cade and Huo.¹⁰ The twelve-electron sodium hydride molecule provides a nontrivial but interesting case, since the correlation effects in second-row hydrides have not previously been studied. In first-row hydrides, the motions of the K -shell pair of electrons are found to be quite distinct from the L shell. A similar phenomenon is expected in second-row hydrides; but the addition of the relatively low-lying M shell permits an assessment of the separability of correlation effects between the M shell and its interactions with the K and L shells.

Section II gives a brief development of MBPT.

Section III presents a discussion of the numerical results, including an analysis of the differences in using a V^N and a V^{N-1} potential for the generation of the excited orbitals.

II. MANY-BODY PERTURBATION THEORY

The usual electrostatic Hamiltonian for a general N -electron system is

$$\mathcal{H} = \sum_{i=1}^N h(\hat{i}) + \sum_{i>j} r_{ij}^{-1} \quad (1)$$

where $h(\hat{i})$ is the total one-electron operator. This is separated into

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V} \quad (2)$$

where \mathcal{H}_0 is the unperturbed Hamiltonian suggested by Silverstone and Yin¹¹ and Huzinaga and Arnau¹²:

$$\mathcal{H}_0 = \sum_{i=1}^N \{h(\hat{i}) + V^N(\hat{i}) + \mathcal{P} [V(\hat{i}) - V^N(\hat{i})] \mathcal{P}\}, \quad (3)$$

which contains the Hartree-Fock effective potential V^N :

$$V^N(1) = \sum_{j=1}^N \int d\tau_2 \chi_j^*(2) r_{12}^{-1} (1 - P_{12}) \chi_j(2). \quad (4)$$

The projector \mathcal{P} in Eq. (3) is defined by

$$\mathcal{P} = 1 - O \quad (5)$$

$$O = \sum_{j=1}^N |\chi_j\rangle\langle\chi_j|, \quad (6)$$

where the N occupied orthonormal orbitals χ (given indices i, j, k, l) are the solutions of

$$[h(1) + V^N(1)] \chi_i(1) = \epsilon_i \chi_i(1). \quad (7)$$

These orbitals are used to construct the Hartree-Fock single determinant

$$\Phi_0 = \mathbf{G}[\chi_1(1) \cdots \chi_N(N)] \quad (8)$$

that satisfies the eigenvalue equation

$$\mathcal{H}_0 \Phi_0 = E_0 \Phi_0, \quad (9)$$

whose eigenvalue E_0 is the sum of the orbital energies of Eq. (7):

$$E_0 = \sum_i \epsilon_i. \quad (10)$$

Finally, the perturbation \mathbf{v} in Eq. (2) is given by

$$\mathbf{v} = \mathcal{H} - \mathcal{H}_0 = \sum_{i < j} r_{ij}^{-1} - \sum_i \{V^N(i) + \mathcal{P}[V(i) - V^N(i)]\mathcal{P}\}. \quad (11)$$

The arbitrary potential $V(i)$ in Eqs. (3) and (11) permits the "virtual" Hartree-Fock orbitals to be modified to alter the convergence of the perturbation series. As suggested by Kelly,¹ a reasonable choice would be a V^{N-1} potential,

$$V(1) \equiv V^{N-1}(1) = \sum_{j=1}^{N-1} \int d\tau_2 \chi_j^*(2) r_{12}^{-1} (1 - P_{12}) \chi_j(2), \quad (12)$$

and this would determine the orbitals (given indices a, b, c, d) that are unoccupied in the Hartree-Fock ground state:

$$\mathcal{P}[h(1) + V(1)]\mathcal{P} \chi_a(1) = \epsilon_a \chi_a(1). \quad (13)$$

Although there is great flexibility in choosing the potential V , the present work is limited to the two cases, V^N and V^{N-1} .

With the perturbation splitting of Eq. (2), the total electronic energy, E , of the system can be written

$$E = E_{\text{SCF}} + E_{\text{corr}} \quad (14)$$

where the SCF energy is given by

$$E_{\text{SCF}} = E_0 + \langle \Phi_0 | \mathbf{v} | \Phi_0 \rangle \quad (15)$$

and the correlation energy is obtained from the "linked-cluster" expansion²:

$$E_{\text{corr}} = \sum_{K=1}^{\infty} \langle \Phi_0 | \mathbf{v} [(E_0 - \mathcal{H}_0)^{-1} \mathbf{v}]^K | \Phi_0 \rangle_L. \quad (16)$$

All of the second- and third-order Goldstone diagrams which must be computed with this choice of \mathcal{H}_0 are given in Fig. 1 where $(-X)$ is the interaction with the negative of the one-particle potential V . The choice of $V \equiv V^N$ for this arbitrary potential causes the six diagrams (O) thru (T) in Fig. 1 to cancel.

Using the rules of Brandow,¹³ which are a combination of the Hugenholtz¹⁴ and Goldstone³ type,

only diagrams (A), (C), (E), (G), (O), and (S) in Fig. 1 need be considered since the others are taken into account due to the antisymmetrized vertices. Specifically, these diagrams are as follows:

$$(A) = \sum_{i>j} \sum_{a>b} \frac{|\langle ij || ab \rangle|^2}{D(ijab)}, \quad (17)$$

$$(C) = \sum_{i>j} \sum_{a>b} \sum_{c>d} \frac{\langle ij || ab \rangle \langle ab || cd \rangle \langle cd || ij \rangle}{D(ijab)D(ijcd)}, \quad (18)$$

$$(E) = \sum_{i>j} \sum_{k>l} \sum_{a>b} \frac{\langle ab || ij \rangle \langle ij || kl \rangle \langle kl || ab \rangle}{D(ijab)D(klab)}, \quad (19)$$

$$(G) = \sum_{ijk} \sum_{abc} \frac{\langle ab || ij \rangle \langle ic || ak \rangle \langle kj || cb \rangle}{D(ijab)D(kjcb)}, \quad (20)$$

$$(O) + (S) = \sum_{i>j} \sum_{abc} \frac{\langle ab || ij \rangle [\sum_n \langle cn || an \rangle - \langle c | V | a \rangle] \langle ij || cb \rangle}{D(ijab)D(ijcb)}, \quad (21)$$

where the integrals are defined to be

$$\langle pq || uv \rangle = \langle pq | uv \rangle - \langle pq | vu \rangle, \quad (22)$$

$$\langle pq | uv \rangle = \int d\tau_1 \int d\tau_2 p^*(1) q^*(2) r_{12}^{-1} u(1) v(2). \quad (23)$$

The energy denominators in Eqs. (17)–(21) are given in terms of the eigenvalues of Eqs. (7) and (13):

$$D(ijab) = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b. \quad (24)$$

However, a more complete description can be obtained by summing many higher-order "diagonal"

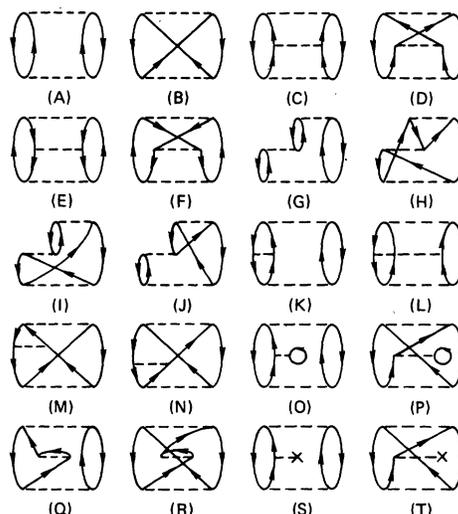


FIG. 1. Second- and third-order Goldstone diagrams contributing to the correlation energy.

type diagrams to all orders by using a convenient denominator shift D^S , as suggested by Kelly¹: namely,

$$D^S(ijab) = D(ijab) + \Delta(ijab), \quad (25)$$

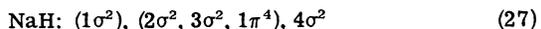
$$\begin{aligned} \Delta(ijab) = & -\langle ab \| ab \rangle - \langle ij \| ij \rangle + \langle ai \| ai \rangle \\ & + \langle aj \| aj \rangle + \langle bi \| bi \rangle + \langle bj \| bj \rangle \\ & - \left(\sum_{n=1}^N \langle an \| an \rangle - \langle a | V | a \rangle \right) \\ & - \left(\sum_{n=1}^N \langle bn \| bn \rangle - \langle b | V | b \rangle \right). \quad (26) \end{aligned}$$

The denominator shift of Eq. (26) when used in second order, Eq. (17), includes the "diagonal" elements of the third-order diagrams and thus the summations in Eqs. (18)–(21) must be restricted accordingly. It should be observed that a shift of this type is equivalent to expanding the perturbation series about a different origin and is thus similar to the theory^{15–17} of Epstein and Nesbet, where the space of all admissible configurations in a given order is used.

Following the philosophy of Sinanoğlu¹⁸ and Nesbet,¹⁹ and the numerical results of Kelly,¹ it is to be expected that the "pair-like" contributions to the correlation energy will dominate the perturbation series; hence, the present numerical results are limited to "pair-like" terms. Diagrams (A), (C), (O), and (S) in Eqs. (17), (18) and (21) are exclusively "pair-like" and are therefore computed without constraints. The pair contribution of diagram (E) occurs when the summation indices of Eq. (19) are restricted to $i=k$ and $j=l$; these terms are summed by means of the denominator shift of Eq. (25). Finally, the pair contribution of diagram (G) is included in the calculation by restricting the sum over k , in Eq. (20), to $k=i$. These constraints entail a neglect of the three-body part of (G) and the nondiagonal contribution in (E). These effects would introduce a relatively small but positive contribution to the correlation energy.^{7,20–22}

III. NUMERICAL RESULTS

The sodium hydride molecule has an interesting electronic structure, which can be represented as follows:



where the groups in parentheses represent the K shell and L shell of the Na atom. Thus, the outer two electrons, $4\sigma^2$, comprising the NaH bond essentially lie outside two completed inner shells of the Na atom and are considered part of the M shell. An analogous structure occurs in LiH,

where the bonding pair lies outside the K shell of the Li atom; in this case, the correlation energy between the K shell and the bonding pair (L shell) amounts to about 1.5 kcal/mole or ~3% of the total correlation.^{23,24} Similarly, for the remainder of the first-row hydrides, the correlation between the K shell and all of the outer electrons (L shell) falls in the range of about 3–5% of the total correlation.^{23–25} With NaH, one can assess the intershell correlation between the K shell, L shell, and outer (or M) shell.

There has been a dearth of calculations performed on second-row molecules; however, Cade and Huo¹⁰ have reported a two-center Slater-type SCF basis set for NaH. The orbital exponents have been extensively optimized to yield an accuracy believed¹⁰ to be within 5×10^{-3} hartrees of the true Hartree-Fock orbitals and to yield reasonably good spectroscopic constants. The basis set is given in Table II of Cade and Huo¹⁰ with the correction of $\zeta = 2.98436$ for the orbital exponent of the $\sigma 2S_{\text{Na}}$ orbital (correction of this misprint in Table II¹⁰ was kindly supplied by P.E. Cade). The basis set consists of a total of 32 orbitals of which 16 are of σ symmetry and 8 are of π and $\bar{\pi}$ symmetries. Since no functions of δ or higher symmetry are included in this set, the correlation energy results are restricted to contributions arising from the σ , π , and $\sigma\pi$ subspaces of the full "virtual" space. Nevertheless, the use of this basis set is expected to produce indicative results while simultaneously permitting a reasonably inexpensive calculation.

Two potentials for the excited orbitals have been used; namely, the usual V^N and a form of Kelly's¹ V^{N-1} where the excited states of a given symmetry are determined by excluding the highest occupied orbital of the same symmetry. The results are presented in Table I for the second-order (E_2)

TABLE I. Pair contributions to the correlation energy of NaH ($E_{\text{SCF}} = -162.3928$, $R = 3.566$ bohr).^a

Potential	V^N	V^{N-1}
$E_2(A)$	-0.2119	-0.2536
$E_2^S(A)$	-0.2415	-0.2483
$E_3^S(C)$	+0.0168	+0.0176
$E_3^S(G)$	-0.0287	-0.0312
$E_3^S(O) + (S)$... ^b	+0.0075
$E_2^S + E_3^S$	-0.2534	-0.2544
Total energy	-162.6462	-162.6472

^a Energies in hartrees.

^b Identically zero for V^N potential.

energy corrections along with the second- and third-order pair contributions (E_2^S and E_3^S) using the denominator shift of Eq. (25).

Although the choice of potential gives very different results for the unshifted E_2 , the differences are much less pronounced for the shifted E_2^S , and even smaller once the entire $E_2^S + E_3^S$ pair calculation is performed. This leveling effect between the two potentials is an interesting feature of MBPT and it arises because one uses *all* the configurations that can contribute to the particular order of perturbation theory. This result is substantially different from conventional configuration-interaction (CI) calculations where, since one necessarily needs to truncate the CI series, an optimum set of orbitals is sought (i.e., a transformation of the virtual space from V^N to V^{N-1} ; or optimally a transformation to Löwdin's natural orbitals²⁶). A similar observation has been reported pertaining to this leveling effect between V^N and V^{N-1} for MBPT calculations by Dutta²⁷; and in the Bethe-Goldstone framework by Van der Velde and Nieuwpoort.²⁸

From an experimental total energy value of $E_{\text{expt}} = -163.026$ hartrees, an approximate relativistic-energy correction of $E_{\text{rel}} = -0.2008$ hartrees, and with E_{SCF} , Cade and Huo¹⁰ have estimated the total correlation energy for NaH to be $E_{\text{corr}} = -0.432$ hartrees. Thus from Table I, it is seen that ~59% of the total correlation energy is recovered using the Cade and Huo basis within the MBPT framework.

A more detailed examination of the correlation-energy contributions can be obtained from Table II where the value of $E_2^S + E_3^S$ is given for the various intrashell and intershell interactions for both the V^N and V^{N-1} potentials. Again, the contributions are seen to be remarkably similar for the two potentials. Of particular interest, of course, is that the *KL* intershell correlation energy amounts to only ~2.4% of the total, *KM* is ~0.014%, and *LM* is ~1.2%, for a total intershell correlation of ~3.6%. Although this is a small percentage of the total correlation energy, the absolute magnitude of these intershell correlations is non-negligible, being approximately 10 kcal/mole.

Table II also shows that the bulk of the correlation energy recovered comes from the "interpair" correlations between the four canonical pairs of the *L* shell, which are indicated in Eq. (27). The *L* shell contains $n = 8$ electrons comprising a total of $n(n-1)/2 = 28$ individual pairs, of which $n/2 = 4$ are the "canonical" pairs, e.g., $2\sigma(\alpha) - 2\sigma(\beta)$; 12 are of the "interpair" variety having parallel spin, e.g., $2\sigma(\alpha) - 3\sigma(\alpha)$; and 12 are of the "interpair" variety having antiparallel spin, e.g., $2\sigma(\alpha) - 3\sigma(\beta)$. Although the magnitudes of the individual "intra-

pair" correlation contributions are larger than the individual "interpair" contributions, the greater number of the latter dictates the numerical superiority. It is noteworthy that these remarks apply equally well to both the V^N and V^{N-1} results.

Since a typical correlation energy per electron pair is expected to be ~1 eV (-0.037 hartrees), correlation in the *M* shell (or NaH bond) appears to be quite adequately described since an energy of -0.034 hartrees is recovered. This is attributable to the abundance of diffuse Na orbitals and the collection of σ and π orbitals located on the H atom in the Cade and Huo basis set. Hence, it is the two-center nature of the basis set that allows a good description of the chemical bond to be obtained.

On the other hand, only about half of the *K*-shell correlation energy is recovered since only two 1s orbitals having high orbital exponents on Na are included in the basis set. This inadequacy could be corrected by the addition of several functions of σ , π , and δ symmetry species, all with high orbital exponents. However, since the *KM* intershell contribution is almost negligible, the *K*-shell electrons are essentially noninteracting with the electrons of the NaH bond. Thus, for many purposes (e.g., the calculation of potential curves and excitation energies of the valence shell electrons), the extreme effort involved in expanding the basis set for the *K* shell would not be warranted.

We estimate that an additional 20% improvement in the total correlation energy could derive from augmenting the basis set with additional diffuse orbitals of π and δ symmetry, since results of this magnitude have been obtained with a similar augmentation of a Cade and Huo basis set for hydrogen fluoride.²⁹ A parallel improvement in the *KL* and

TABLE II. Decomposition of $E_2^S + E_3^S$ pair-correlation energies (in hartrees) of NaH into intrashell and intershell contributions.

Potential	V^N	V^{N-1}
Intrashell <i>K</i>	-0.019 94	-0.019 94
<i>L</i> (intrapair)	-0.052 78	-0.052 98
<i>L</i> (interpair)	-0.130 78	-0.131 72
<i>L</i> (total)	-0.183 56	-0.184 70
<i>M</i>	-0.034 08	-0.034 04
<i>K + L + M</i>	-0.237 58	-0.238 68
Intershell <i>KL</i>	-0.010 48	-0.010 43
<i>KM</i>	-0.000 06	-0.000 06
<i>LM</i>	-0.005 25	-0.005 27
<i>KL + KM + LM</i>	-0.015 79	-0.015 75
Total	-0.253 37	-0.254 43

LM intershell interactions would be expected to accompany this basis-set alteration. This would bring the total intershell contribution up to about -0.024 hartrees (~ 15 kcal/mole), representing $\sim 5.4\%$ of the total correlation.

The present work shows that the use of virtual orbitals determined from either a V^N or a V^{N-1} potential gives pair correlation energies that differ by less than 0.6 kcal/mole. This suggests that the use of a V^{N-1} potential could be eliminated in MBPT calculations of pair-correlation energies. Also, the results show that there is a clear sepa-

ration of correlation effects into intrashell and intershell contributions, but that with respect to the canonical pairs within a shell, both intrapair and interpair effects are important.

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