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Energy of CH Calculated by Many-Body Perturbation Theory*

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The many-body perturbation theory of Brueckner and Goldstone has been used to calculate the total nonrelativistic energy of the CH molecule. We have used a single-center expansion with a complete set of basis states appropriate to the neutral carbon atom. At the equilibrium internuclear separation we calculate the total energy for CH to be −38.482 ± 0.02 a.u. as compared with the experimental value −38.479 a.u. We have also calculated a full potential curve for the $^2\Pi$ ground state of CH accurate to second order in the perturbation expansion.

I. INTRODUCTION

Recently attempts have been made to apply many-body perturbation theory[1,2] to molecules using single-center wave functions.[3–5] These have involved calculations of the total (nonrelativistic) molecular energy, and in the hydrides treated so far good results have been obtained, the errors in the total energy being 1 eV or less. With this in view, it is of interest to investigate the usefulness of these techniques for other properties, particularly those that depend on the molecular geometry. The choice of basis set and starting point for the perturbation expansion critically affect the convergence of the calculations, which may vary for different molecular properties.

In a previous paper[6] we analyzed the different types of diagrams that can occur into three classes; those that contribute solely to the Hartree-Fock energy, those correlation-energy terms which are independent of internuclear separation, and correlation-energy terms dependent upon internuclear separation. This paper will also consider the separate convergence characteristics of these three types of diagrams. With these points in mind, we have performed calculations on CH starting from a complete set (including continuum) of carbon basis functions. This set has previously been employed for a calculation of the correlation energy of carbon,[7] and thus will allow a comparison of the two calculations, as well as a direct calculation of the correlation-energy difference between atoms and molecule.

In this paper we use the Born-Oppenheimer approximation and neglect relativistic effects. We start with a carbon nucleus at the origin, seven electrons, and a hydrogen nucleus at a distance R from the origin. The electron states are calculated in the V^{N-1} potential appropriate to neutral carbon,[7] i.e., electron states are calculated in a potential with a carbon nucleus and six other electrons. Interactions with the extra electron and with the hydrogen nucleus are included as perturbations along with the usual correlation perturbations. This approach was used successfully in our previous H_2O calculations.[5] The success of such an approach depends upon a reasonable degree of cancellation between the interactions with the extra electron and with the hydrogen nucleus. Such cancellations are expected for CH since the Hartree-Fock (HF) single-particle energies of $\epsilon_{3\sigma}$ and $\epsilon_{1\pi}$ are $-0.455\,22$ and $-0.414\,97$ a.u., respectively,[8] as compared with HF ϵ_{2p} for carbon[7] which is $-0.433\,33$ a.u. In these calculations

$$H_0 = \frac{6}{R} + \sum_{i=1}^{7}\left(-\frac{\nabla_i^2}{2} - \frac{6}{r_i} + V(r_i)\right), \qquad (1)$$

where $V(r_i)$ is the V^{N-1} for neutral carbon,[7] and the perturbation

$$H' = \sum_{i<j=1}^{7} |\vec{r}_i - \vec{r}_j|^{-1} - \sum_{i=1}^{7}\left[V(r_i) + |\vec{r}_i - \vec{R}|^{-1}\right], \qquad (2)$$

where $\vec{R}$ is the position of the hydrogen nucleus. Our unperturbed state Φ_0 corresponding to the $^2\Pi$ ground state of CH is then the determinant for the atomic configuration $(1s)^2\,(2s)^2\,(2p\sigma)^2\,(2p\pi)$. Our unperturbed energy is equal to $6R^{-1} + \sum_{i=1}^{7}\epsilon_i$.

We then use many-body perturbation theory to calculate the higher-order terms in the energy expansion. These terms may then be evaluated by sums over the excited states as described previously.[9,10] We sum over continuum states by numerical integration and we include the infinite number of bound excited states by the n^{-3} rule.[9] Also, certain classes of terms may be summed by appropriate denominator shifts or by approximate geometric sums.[9,10] These methods were also used in the calculations of Refs. 3–5.

The first-order corrections for the energy are shown in Fig. 1. The diagram of Fig. 1(d) represents interaction with the hydrogen nucleus, i.e., matrix elements of $-|\vec{r}_i - \vec{R}|^{-1}$. The second-or-

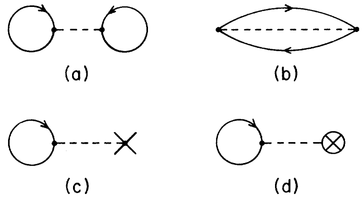

FIG. 1. First-order corrections to the unperturbed energy. Cross represents interaction with minus the single-particle potential. Circled cross represents interaction with hydrogen nuclei.

der corrections which involve only single excitations are shown in Fig. 2(a). The dashed line terminated by an open circle represents the net interaction with passive unexcited states, minus the single-particle potential, and the hydrogen nucleus. It represents matrix elements of the operator Ω given by

$$\langle a | \Omega | b \rangle = \sum_{n=1}^{N} (\langle an | v | bn \rangle - \langle an | v | nb \rangle) - \langle a | V | b \rangle - \langle a | |\vec{r} - \vec{R}|^{-1} | b \rangle . \quad (3)$$

Third-order diagrams involving Ω are given in Figs. 2(b)–2(k). It may be shown that diagrams 2(a)–2(e) and the inverse diagrams to 2(f) and 2(g) contribute to the HF energy. Diagrams 2(f)–2(k) contribute to the correlation energy and are dependent upon the internuclear separation through the operator Ω. In Fig. 3 are shown second- and third-order diagrams which contribute to the correlation energy and are independent of internuclear separation. Diagrams 3(a) and (b) are the usual second-order pair correlation diagrams. Diagrams 3(c)–3(i) are the third-order three-body diagrams.

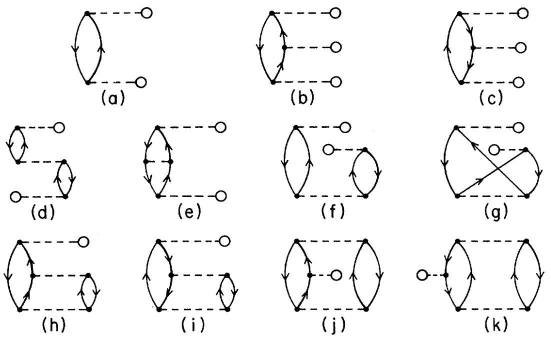

FIG. 2. Second- and third-order diagrams involving the net interaction with passive unexcited states, minus the single-particle potential, and the hydrogen nuclei. This sum of operators is represented graphically by a dashed line with an open circle at one end. Graphs (f)–(i) can be inverted, and the exchanges of graphs (h)–(k) should also be included. The inverse of graphs (f) and (g) contribute to the Hartree-Fock energy.

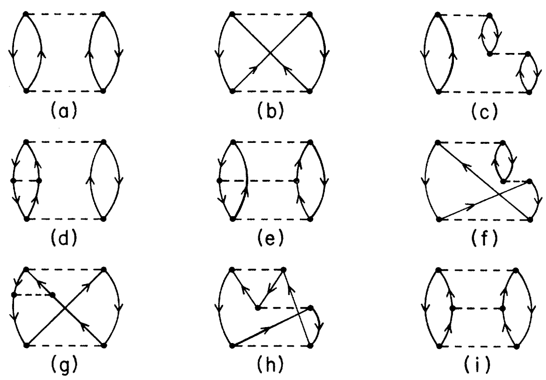

FIG. 3. (a) and (b) Second-order correlation-energy diagrams; (c)–(i) third-order three-body correlation-energy diagrams.

II. RESULTS

Figure 4 shows the results of our second-order calculations which contribute to the HF energy and also the HF curve of Cade and Huo[8] for comparison. As expected, at large distances the convergence is slow, and the errors are relatively large. However, even in second order the calculated inter-

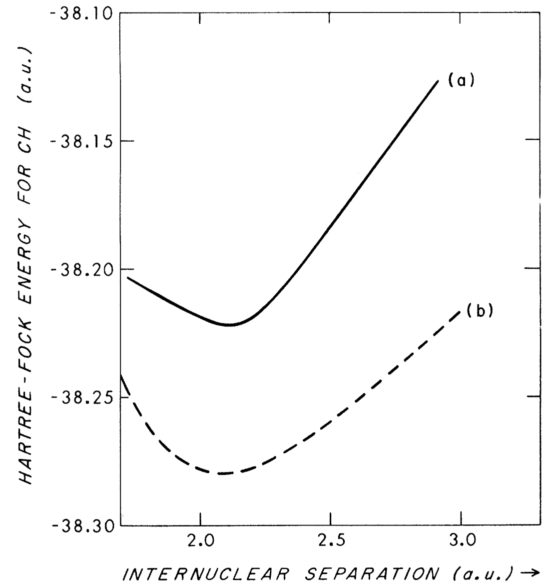

FIG. 4. Hartree-Fock energy of CH as a function of internuclear separation. (a) Second-order single-center calculation, this paper. Diagrams of Figs. 1 and 2(a) are included. (b) Accurate linear-combination-of-atomic-orbitals Hartree-Fock calculation from Ref. 8. As described in the text, calculations of third-order diagrams at $R = 2.12$ a.u. bring our results into excellent agreement with curve (b).

TABLE I. Results of third-order Hartree-Fock calculations (in a.u.). Diagrams of Figs. 1 and 2(a)–2(e) and the inverses of Figs. 2(f) and 2(g) are included.

	$R=2.12$ a.u.	$R=2.92$ a.u.
First order	−0.471530	−0.389771
Second order	−0.236254	−0.227160
Diagram 2(b)	−0.063524	−0.019402
2(c)	−0.006602	−0.064815
2(d)	+0.016988	+0.024841
2(e)	−0.008779	−0.016236
2(f)[a]	−0.008494	+0.012421
2(g)[a]	−0.003058	−0.004850
Total third order	−0.056571	−0.068041
HF energy through third order	−38.2792	−38.1947
Exact HF energy[b]	−38.2794	−38.2236

[a] Inverses only. [b] References 8 and 12.

nuclear distance 2.10 a.u. is close to the experimental value[11] of 2.116 a.u. The second-order curve is by no means parallel to the HF curve and the calculated vibration frequency is rather different (4078 cm^{-1} vs the HF value[8] of 3108 cm^{-1}). Whether this is a general phenomenon or peculiar to CH only, further calculations can tell. However, the effects of the perturbation would be expected to be the same for all diatomic hydrides.

We can improve the results of the second-order calculations by going to higher orders, and Table I shows the results of the third-order HF calculation at two distances, 2.12 and 2.92 a.u. [we include diagrams 2(b)–2(e) and the inverses of 2(f) and 2(g)]. At the experimental distance our result through third-order is within 0.0002 a.u. of the HF value.[8] While this very close agreement may be somewhat fortuitous, it does demonstrate the rapid convergence of the perturbation series at the experimental internuclear distance. At 2.92 a.u., the convergence is somewhat slower, and our third-order result is still 0.03 a.u. away from the HF limit value. In previous papers[3,5] some of the contributions from higher orders has been approximated by geometrical summations. If we do this here, we find energies of −38.2969 and −38.2246 a.u. for the two distances under consideration. While this gives almost exactly the HF value at 2.92 a.u., it is 0.017 a.u. lower than the corresponding value at 2.12 a.u. This suggests that such a simple geometrical approximation cannot be used along the potential curve with consistency. We estimate the error in our third-order HF calculation to be ± 0.005 a.u.

The lowest-order diagrams corresponding to the correlation energy are shown in Figs. 3(a) and 3(b), and Table II shows the results for these contributions to the pair-correlation energies. Since we start from an atomic basis set, many of these terms are exactly the same as in the atom, and Table II also shows the differences between atom and molecule. Since we have not yet considered diagrams such as Figs. 2(b)–2(k), these differences do not correspond to the effects of molecular potential, but solely to the presence of the extra electron. Thus the differences are due firstly to the extra pair energy $\sum_n E_{\mathrm{corr}}(n, 2p_0^-)$, and secondly to the fact that excitations to $2p_0^-$ particle states are no longer possible. We must now consider the effects of molecular potential and of higher-order diagrams. A large part of the effect of the molecular potential is given by the sum of diagrams 2(f) and 2(g), 0.005436 a.u. Diagrams of Figs. 2(h)–2(k) were calculated for H_2O and found to be quite small; furthermore, they cancel among themselves to give a final result of approximately 10% of any one diagram.

We have calculated the magnitude of diagram 2(k) (omitting $2p$ particle states) to be −0.00468, and thus the net effects of these four diagrams to be a maximum of 0.001 a.u. However, these diagrams are not small when the particles are $2p$ states. To take proper account of these diagrams and their higher-order counterparts, as well as the third-order correlation diagrams shown in Fig. 3, shifted denominators may be used.[7] These result in a reduction of the $2s/2s$ pair-correlation energy by 0.0045 a.u. and of the $2s/2p$ pairs by 0.0011 a.u. We must also include the fourth-order rearrangement diagrams which couple the pair energies together.[7] These reduce the total excess pair-correlation energy by 0.001 a.u. Lastly, three-body effects must be taken into account. The previous calculations on carbon[7] demonstrated that the important three-body effects were those involving $2s$ and $2p$ electrons. There are ten such triples in CH compared to only six in the atom, and we estimate the contribution of these terms to the excess correlation energy to be 0.005 a.u. The

TABLE II. Second-order pair-correlation energies (a.u.) [see Figs. 3(a) and 3(b)].

Electron pair	CH	C	Difference
$1s/1s$	−0.04036	−0.04066	+0.00030
$1s/2s$	−0.00645	−0.00648	+0.00003
$1s/2p$	−0.00966	−0.00645	−0.00321
$2s/2s$	−0.04075	−0.04230	+0.00155
$2s/2p$	−0.09314	−0.07237	−0.02077
$2p/2p$	−0.05319	−0.01069	−0.04250
Total	−0.24355	−0.17895	−0.06460

TABLE III. Contributions to the correlation-energy difference. All these results are the differences between the corresponding effects for CH and C.

Pair difference	−0.064 60
Change in $2s/2s$	+0.004 50
Change in $2s/2p$	+0.001 11[a]
Diagrams 2(f)−2(g)	+0.005 44
Diagrams 2(h)−2(k)	+0.001
Pair coupling	+0.001
Three-body effects	+0.005[b]
Total	−0.0466

[a] Inclusions of denominator shifts to account for effects from molecular potential and other higher-order diagrams.

[b] Estimated.

contributions to the correlation-energy differences are summarized in Table III. Our final value of the correlation-energy difference is −0.047 a.u., and we estimate the error limits, which arise largely from fourth- and higher-order diagrams to be ±0.006 a.u., about 10% of the total value. The correlation energy of CH has been determined by Liu and Verhaegen[12] as −0.199 a.u., giving an "experimental" correlation-energy difference of −0.043 a.u. Thus our calculated value of the correlation-energy difference between CH and C is only 10% in error, which reflects the fast convergence of the perturbation series at the equilibrium internuclear distance. This fast convergence arises because the effects of the extra electron and the hydrogen nucleus almost cancel.

An analysis of the various contributions to the correlation-energy difference gives some insight into different methods that have been used for its calculation. Diagrams 2(f)−2(k) represent the change in pair-correlation energy owing to the molecular potential; that is, they correct for the use of atomic orbitals instead of the molecular HF orbitals. The changes in $2s/2s$ and $2s/2p$ pair-correlation energy in Table III, and of the $2s/2s$ in Table II, are closely analogous to the "near degeneracy effects" of Clementi and Veillard,[13] except that small higher-order terms have been included.

It should also be possible to calculate correlation-energy differences along the potential curve by considering the diagrams of Figs. 2(f)−2(k). It is well known that HF wave functions dissociate to mixtures of atoms and ions and thus the correlation energy increases at first as the internuclear distance increases from the equilibrium distance. We have calculated the correlation energy (CE) at $R=2.92$ a.u. using the same approximations that were employed at $R=2.12$ a.u. The difference between the two results, CE(2.92) − CE(2.12), is −0.0002 a.u. This result is smaller than the higher-order terms that have been neglected, and much smaller than the approximate "experimental" value of −0.013 a.u. obtained by using a Morse curve. This reflects the slower convergence of all diagrams involving Ω that was also observed in the calculation of the HF energy at $R=2.92$ a.u. In fact one of the most important effects that has been neglected is the effect of molecular potential on the three-body terms. At large internuclear distances, when one of the orbitals is almost entirely H(1s), the three-body terms will be very much the same as those in the carbon atom. Since our estimate of the excess three-body term in CH over carbon was 0.005 a.u., this represents an appreciable part of the correlation-energy change along the potential curve.

III. CONCLUSIONS

Our results for the HF energy of CH at the equilibrium internuclear separation, −38.279 a.u., and for the correlation-energy difference between CH and the carbon atom, −0.047 a.u., are both in reasonable agreement with experiment. Our total energy of −38.482 a.u. for CH compares favorably with the value −38.440 a.u. obtained in a configuration-interaction calculation by Bender and Davidson.[14] The convergence of the perturbation series appears to be rapid at the equilibrium internuclear separation, but this does not seem to be true at larger values of R. The reasonable degree of convergence is indicated in Table IV which lists results of various calculations on molecules using single-center basis sets and many-body perturbation theory of the equilibrium internuclear separation. At larger values of R the single-center functions should become less valid for the unperturbed wave function.

Since the second-order HF potential curve of Fig. 4 gives an equilibrium separation close to the experimental value, this indicates the possible use of such calculations for those cases where the potential curve is unknown. Such calculations could

TABLE IV. Molecular energies (in a.u.) from many-body perturbation-theory calculations.

Molecule	Calculated[a]	Experimental
CH	−38.482 ± 0.02	−38.479[b,c]
H_2O	−76.48 ± 0.07[d]	−76.481
HF	−100.4186[e]	−100.4485
H_2	−1.176[f]	−1.1745

[a] Nonrelativistic total energy calculated at the equilibrium internuclear separation.

[b] Reference 11.

[c] Reference 12.

[d] Reference 5.

[e] Reference 4.

[f] Reference 3.

be carried out for the ground state and excited states. Energy differences between the potential curves could then be obtained. The rapid convergence of the perturbation expansion confirms the acceptability in this case of using carbon rather than nitrogen, the united atom, as a starting point. We plan to use these methods to calculate many additional properties of CH.

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Locality of the Effect of the Pauli Principle in Atoms

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It is shown that the conventional application of the Pauli principle to the qualitative estimation of the relative distributions of electrons with parallel and antiparallel spins is wrong. The Pauli principle induces a local reduction of the probability of finding electrons with parallel spins close together. However, for neutral atoms at least, such electrons have a considerably higher probability of being found at moderate separations and an accompanying reduced probability of being found at higher separations, relative to electrons with antiparallel spins.

The Pauli principle is usually invoked to argue that in atoms and molecules electrons with parallel spins tend to stay essentially further away than electrons with antiparallel spins. This argument should lead to expectation values of $1/r_{12}$ being lower and of r_{12} and r_{12}^2 being higher for the higher multiplicity terms. The interpretation of Hund's rule in terms of the different contributions to the total energy has recently been attempted.[1-4] It has been noticed that, contrary to the customary assumption, the interelectronic repulsion in the higher multiplicity terms is higher than that in the lower multiplicity terms.[1,2] This has been shown to be generally valid for light neutral atoms[4]; for sufficiently highly charged isoelectronic ions the conventionally expected ordering of interelectronic repulsions is generally observed. It has been argued[3] that higher $\langle 1/r_{12}\rangle$ for the higher multiplicity terms does not exclude the possibility of $\langle r_{12}\rangle$ being higher for them, and that it is this latter value which measures the average interelectronic distance. Very recently, accurate calculations for the $^{1,3}P$ terms of the He isoelectronic sequence have become available.[5] They indicate just the trends discussed in Ref. 4. In particular, the values of $(^3C - {}^1C)/(^3L - {}^1L)$, where C denotes the interelectronic repulsion and L the nuclear attraction, are observed to increase from a negative value for the neutral He atom to positive values for the higher members of the isoelectronic sequence. The asymptotic behavior expected on the basis of a perturbation-theoretic argument,[4] namely, $\Delta C/\Delta L = 1 - \alpha/Z$, α being a constant, is confirmed by these values, presented in Fig. 1. A further check of the results presented in Ref. 5 reveals the hitherto entirely unexpected ordering of $\langle r_{12}\rangle$ and $\langle r_{12}^2\rangle$. Whereas $\langle 1/r_{12}\rangle$ becomes lower for the triplet at $Z = 4$, $\langle r_{12}\rangle$ persists in being