

## Diagrammatic perturbation theory. The ground state of the carbon monosulfide molecule

Stephen Wilson

Citation: [The Journal of Chemical Physics](#) **67**, 4491 (1977); doi: 10.1063/1.434590

View online: <http://dx.doi.org/10.1063/1.434590>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/67/10?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Ground states of the Mo<sub>2</sub>, W<sub>2</sub>, and CrMo molecules: A second and third order multireference perturbation theory study](#)

J. Chem. Phys. **127**, 074306 (2007); 10.1063/1.2768529

[Diagrammatic perturbation theory: An application to the LiH and FH molecules using a universal even-tempered basis set](#)

J. Chem. Phys. **77**, 3674 (1982); 10.1063/1.444269

[Diagrammatic perturbation theory: An application to the nitrogen, carbon monoxide, and boron fluoride molecules using a universal even-tempered basis set](#)

J. Chem. Phys. **72**, 2159 (1980); 10.1063/1.439312

[Diagrammatic perturbation theory applied to the ground state of the water molecule](#)

J. Chem. Phys. **67**, 5552 (1977); 10.1063/1.434751

[Perturbation Treatment of the Ground State of the Hydrogen Molecule](#)

J. Chem. Phys. **47**, 1256 (1967); 10.1063/1.1712076

---

An advertisement for AIP Applied Physics Reviews. It features a blue background with a molecular structure on the left. The text 'NEW Special Topic Sections' is prominently displayed in white. Below it, 'NOW ONLINE' is written in orange, followed by 'Lithium Niobate Properties and Applications: Reviews of Emerging Trends' in white. The AIP Applied Physics Reviews logo is in the bottom right corner.

**NEW Special Topic Sections**

**NOW ONLINE**  
Lithium Niobate Properties and Applications:  
Reviews of Emerging Trends

**AIP** Applied Physics Reviews

# Diagrammatic perturbation theory. The ground state of the carbon monosulfide molecule

Stephen Wilson<sup>a)</sup>

NASA Institute for Space Studies, Goddard Space Flight Center, New York, New York 10025<sup>b)</sup>  
(Received 21 June 1977)

Diagrammatic many-body perturbation theory is employed in a study of the ground state of the carbon monosulfide molecule for bond lengths close to the equilibrium value. The calculations are complete through third order in the energy within the algebraic approximation. Two different zero-order Hamiltonians are considered and all two-, three-, and four-body terms are determined for the corresponding perturbation expansions. Many-body effects are found to be very important. Padé approximants to the energy expansion are constructed and upper bounds are evaluated. Almost 53% of the estimated correlation energy is recovered. The variation of components of the correlation energy with nuclear separation is investigated. Spectroscopic constants are also calculated.

## I. INTRODUCTION

Diagrammatic perturbation theory<sup>1-4</sup> provides a simple, yet accurate, description of corrections to independent electron models in terms of Feynman diagrams. Each of these diagrams corresponds to a term in the Rayleigh-Schrödinger perturbation expansion and has a simple physical interpretation in terms of the particle-hole formalism. Diagrammatic many-body perturbation theory may be applied to arbitrary molecular systems by invoking the algebraic approximation.<sup>5,6</sup> In this paper, we present the results of calculations for the carbon monosulfide molecule obtained within this approximation. Results are reported for a number of nuclear geometries close to equilibrium. This appears to be the first application to a molecule containing a second-row atom and a second nonhydrogenic atom. The purpose of the present work is to examine the accuracy with which such systems can be treated using diagrammatic perturbative expansions. We examine not only the total energy and its components but also calculate the equilibrium bond distance,  $r_e$ , and the fundamental frequency of vibration. The convergence of the perturbation expansions corresponding to two different zero-order Hamiltonians is discussed.

The very brief outline of diagrammatic perturbation theory given in the following section serves to introduce notation. More detailed discussions can be found elsewhere.<sup>3-6</sup> In the third section the computational aspects of this study are described. The results are presented and discussed in the fourth section. This is followed by some concluding remarks.

## II. DIAGRAMMATIC RAYLEIGH-SCHRÖDINGER PERTURBATION THEORY

In addition to providing an attractive pictorial description of electron correlation effects in atoms and molecules, the diagrammatic perturbation expansion when taken through third order in the energy forms the basis of a noniterative and computationally efficient

algorithm<sup>6-8</sup> for electronic structure calculations to an accuracy well beyond that afforded by the Hartree-Fock model.

The correlation energy is represented by the diagrams shown in Fig. 1. In this figure, diagrams which are related by electron exchange have been omitted. The first diagram describes second-order effects; the remaining diagrams are of third order. The expressions corresponding to each of these diagrams are easily written down.<sup>5</sup> The diagrams may be given a very simple physical interpretation in terms of the particle-hole formalism. The second-order diagram represents the excitation of a pair of electrons and then the return to the vacuum state. Each of the third-order diagrams represents the excitation of a pair of electrons, an interaction between the holes, created below the Fermi level, and the particles, created above the Fermi level, and then the return to the vacuum state. The three third-order diagrams differ in the nature of the central interaction line: a hole-hole interaction, a hole-particle interaction or a particle-particle interaction. The second-order and third-order "particle-particle" diagrams are said to describe two-body effects since they contain only two hole (upward directed) lines. The third-order "hole-particle" diagram can describe two- and three-body effects, while the "hole-hole" diagram can describe components of the correlation energy involving up to four bodies.

In this work, we shall denote a component of the correlation energy by  $E_c^a$  where  $a$  denotes the number of bodies involved and  $b$  the order of perturbation.  $E_b$  will denote the total  $b$ th order energy but  $E^a$  will denote the total  $a$ -body correlation energy through third order.  $E(c)$  will be used to denote the total energy through  $c$ th order.

Two different zero-order Hamiltonian operators<sup>4,6</sup> are employed in this work: the matrix Hartree-Fock

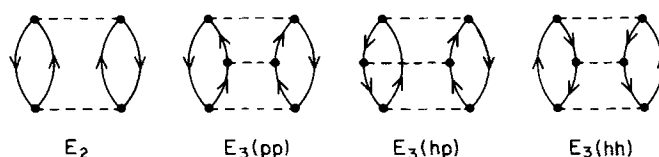


FIG. 1. Second- and third-order diagrams.

<sup>a)</sup>National Research Council Resident Research Associate, supported by the National Aeronautics and Space Administration.

<sup>b)</sup>Present address: Science Research Council, Daresbury Laboratory, Daresbury, Warrington WA4 4AD, England.

TABLE I. Basis set of Slater exponential functions used to parameterize orbitals.<sup>a</sup>

C:	1s(5.3767, 8.982), 2s(2.013, 5.6319, 1.3089), 2p <sub>σ</sub> (1.8076, 2.2398, 0.9554, 6.3438), 3d <sub>σ</sub> (2.65), 4f <sub>σ</sub> (2.06), 2p <sub>π</sub> (1.42, 2.5873, 0.9554, 6.3438), 3d <sub>π</sub> (2.207), 4f <sub>π</sub> (2.9), 3d <sub>δ</sub> (2.207), 4f <sub>δ</sub> (2.9).
S:	1s(13.7174, 17.6913), 2s(6.7527, 14.0693), 3s(2.6107, 1.6426, 5.7425), 2p <sub>σ</sub> (7.1763, 13.53), 3p <sub>σ</sub> (2.3277, 1.3194, 5.4397), 3d <sub>σ</sub> (2.9), 4f <sub>σ</sub> (2.1), 2p <sub>π</sub> (7.1763, 13.5), 3p <sub>π</sub> (2.3277, 1.3194, 5.4397), 3d <sub>π</sub> (2.9), 4f <sub>π</sub> (2.1), 3d <sub>δ</sub> (2.9), 4f <sub>δ</sub> (2.2).

<sup>a</sup>Orbital exponents are given in parenthesis.

*model* Hamiltonian and the *shifted* Hamiltonian. The latter is the sum of the components of total Hamiltonian which are diagonal in the Hartree–Fock basis. Energy values resulting from the corresponding perturbation expansions will be distinguished by placing a bar on those derived from the *shifted* Hamiltonian.

From the third-order expansion for the energy we can construct the [2/1] Padé approximant<sup>9</sup>

$$E[2/1] = E_0 + E_1 + E_2 / \left(1 - \frac{E_3}{E_2}\right). \quad (1)$$

This approximant has certain invariance properties which are not shared by the usual Taylor series. In particular, it is invariant to changes of scale and to shifts of origin in the reference spectrum<sup>9</sup>

It is well known that the calculation of the energy through third order is equivalent to the calculation of the wave function through first order. By substituting the first-order wave function

$$\phi_0 + \gamma\phi_1 \quad (2)$$

in the Rayleigh quotient, we obtain an upper bound to the energy

$$E_{\text{u.b.}} = E_0 + E_1 + ((2\gamma - \gamma^2)E_2 + \gamma^2 E_3) / (1 + \gamma^2 S), \quad (3)$$

where  $\gamma$  is a parameter whose optimal value may be determined by invoking the variation theorem and  $S$  is the normalization integral

$$S = \langle \phi_1 | \phi_1 \rangle. \quad (4)$$

### III. COMPUTATIONAL ASPECTS

The basis set of real Slater exponential functions employed in the present study to parameterize the one-electron functions is given in Table I. It consists of 59 functions; 25 of  $\sigma$  symmetry, 26 of  $\pi$  and  $\bar{\pi}$  symmetry and 8 of  $\delta$  and  $\bar{\delta}$  symmetry. Twenty-seven of the basis functions are centered on the carbon atom and the remaining 32 on the sulfur atom. At a nuclear separation of 2.89964 bohr a matrix Hartree–Fock energy of  $-435.34627$  hartree was obtained. This basis set was employed at all nuclear geometries considered in this work.

The computations were executed on the IBM 360/95 computer at the Goddard Institute for Space Studies. Integrals over Slater basis functions and the matrix Har-

tree–Fock computations were performed using the ALCHEMY programs.<sup>10</sup> The perturbation expansions were evaluated using the FORTRAN programs described elsewhere.<sup>7,8</sup> Starting from integrals over the matrix Hartree–Fock orbitals, the calculation of all terms through third order in both perturbation expansions considered here required approximately 40 min of computer time for each nuclear geometry.

## IV. RESULTS AND DISCUSSION

### A. Calculation at the equilibrium nuclear geometry

#### 1. Convergence of the perturbation expansions

The convergence of the *model* and *shifted* perturbation expansions is contrasted in Table II for an internuclear distance of 2.89964 bohr. The convergence is shown both as a function of the number of interacting bodies and as a function of the order of perturbation. The values of  $E^n$ ,  $n=2,3,4$ , are complete through third order. All contributions of order  $n$  are included in the values of  $E_n$ ,  $n=0,1,2,3$ . The ratio of  $E_3$  to  $E_2$  may be used as a qualitative measure of the rate of convergence of the perturbation expansions. Since,

$$E_3/E_2 = 0.020 \text{ and } \bar{E}_3/\bar{E}_2 = -0.265, \quad (5)$$

we conclude that the *model* perturbation expansion is probably the more rapidly convergent of the two studies here. Three- and four-body components of the energy are also smaller in the *model* perturbation expansion than in the *shifted* scheme.

#### 2. Calculated correlation energy

The total calculated correlation energies through third order,  $E_2 + E_3$  and  $\bar{E}_2 + \bar{E}_3$ , differ by 0.04772 hartree. By forming the respective [2/1] Padé approximants the difference between the *model* and *shifted* energies is reduced to 0.01630 hartree. On forming this approximant the correlation energy corresponding to the *model* scheme is changed by only 0.00018 hartree while that corresponding to the *shifted* expansion is changed by 0.03160 hartree. The upper bounds to the correlation energy obtained from the two perturbation expansions

TABLE II. Convergence of the perturbation expansion at  $R=2.89964$  bohr.<sup>a</sup>

$\hat{\mathcal{H}}_0$	$\hat{\mathcal{H}}_{\text{model}}$	$\hat{\mathcal{H}}_{\text{shifted}}$
(i) with increasing number of bodies		
$E^0$	+33.1076	+33.1076
$E^1$	-271.2324	-468.3463
$E^2$	-197.7513	-0.5595
$E^3$	+0.0588	+0.1302
$E^4$	+0.0059	+0.0119
(ii) with increasing order		
$E_0$	-238.1248	-468.4538
$E_1$	-197.2214	0.0
$E_2$	-0.4563	-0.5682
$E_3$	-0.0089	+0.1507

<sup>a</sup>Atomic units are used throughout this table.

TABLE III. Comparison of empirically estimated correlation energy with calculated values.<sup>a</sup>

Reference operator	$\hat{\mathcal{H}}_{model}$	$\hat{\mathcal{H}}_{shifted}$
$E_{\text{empirical correlation}}$	0.880	0.880
$E_{\text{empirical relativistic}}$	1.0646	1.0646
$E_2 + E_3$	0.4652 (52.8%)	0.4174 (47.4%)
$E[2/1]$	0.4653 (52.9%)	0.4490 (51.0%)
$E_{u.b.}$	0.4178 (47.5%)	0.3903 (44.3%)

<sup>a</sup>Atomic units are used throughout; percentages of the empirical correlation energy are given in parenthesis.

differ by 0.02745 hartree; the value obtained from the *model* expansion being the lower.

An empirical estimate of the exact correlation energy may be obtained as follows: The energies of the separated atoms are known to be  $C(^3P)$ :  $-37.8558$  hartree and  $S(^3P)$ :  $-399.144$  hartree.<sup>11</sup> The relativistic energies associated with the carbon and sulfur atoms are  $-0.01381$  and  $-1.05076$  hartree, respectively.<sup>11</sup> The dissociation energy,  $D_0$ , is found to be  $7.85$  eV<sup>12</sup> and the fundamental frequency of vibration is  $1285.08$  cm<sup>-1</sup>.<sup>13</sup> If we assume that the relativistic energy, being mainly attributable to the tightly bound core electrons, does not change on molecule formation, then a total non-relativistic energy of  $-436.22662$  hartree is obtained at the equilibrium geometry. The matrix Hartree-Fock energy obtained in the present study is probably well above the Hartree-Fock limit, however we shall use our present value of  $-435.34627$  hartree to obtain an empirical estimate of the correlation energy of  $0.88035$  hartree. This estimate is compared with our calculated values in Table III.

### 3. Components of the calculated correlation energy

An analysis of the calculated correlation energy at a nuclear separation of  $2.89964$  bohr is presented in Table IV for the perturbation expansions corresponding to both the *model* and the *shifted* reference Hamiltonians. The relative importance of the various terms is evident. The second-order energy is entirely two body and in the *model* expansion it accounts for 98.1% of the calculated correlation energy through third order. On the other hand, in the perturbation expansion based on the *shifted* reference Hamiltonian, the second-order energy overestimates  $\bar{E}_2 + \bar{E}_3$  by 36.1%. In the *model* expansion the third-order two-body component is of opposite sign to the three- and four-body terms; the magnitude of these components is 80% and 8% of the third-order two-body contribution, respectively. In contrast, in the *shifted* expansion the three- and four-body terms have a magnitude which exceeds that of the third-order two-body component. Note that in the *model* expansion the components of the third-order energy are rather large when

compared with the total third-order energy. This indicates the danger of using schemes which do not evaluate all terms through a given order.

The dominant many-body term arises from the third-order ring diagram. For the *model* expansion the third-order ring energy corresponds to 95% of the total three-body energy through third order; for the *shifted* scheme the third-order ring energy corresponds to about 96% of the three-body energy.

### 4. Qualitative analysis of the correlation energy using the second-order pair energies

Since the second-order energy in the *model* perturbation expansion accounts for over 98% of the calculated correlation energy through third order, it can be used as a basis for a qualitative analysis of the correlation energy in terms of two-body effects.

Carbon monosulfide is described in the Hartree-Fock model by the orbital configuration

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 1\pi^2 2\pi^2.$$

The  $1\sigma$  and  $2\sigma$  orbitals may be identified with the sulfur and carbon core electrons. The  $3\sigma$ ,  $4\sigma$ , and  $1\pi$  orbitals are associated with the eight electrons in the sulphur  $L$  shell. The remaining ten electrons, described by the  $5\sigma$ ,  $6\sigma$ ,  $7\sigma$ , and  $2\pi$  orbitals, are of valence type. Thus the 22 electrons in the carbon monosulfide molecule may be divided into 4 groups. Two electrons are associated with the sulfur atom core and 2 with the carbon atom core; 8 electrons are asso-

TABLE IV. Analysis of the correlation energy calculated at the equilibrium nuclear separation,  $R = 2.89964$  bohr.<sup>a</sup>

Component	Reference Hamiltonian	
	<i>Model</i> Hamiltonian	<i>Shifted</i> Hamiltonian
$E_2$	-0.45629	-0.56818
$E_3(pp)$	+0.08336	+0.06919
$E_3^2(hp)$	-0.21400	-0.06053
$E_3^3(hp)$	+0.05579	+0.12458
$E_3(hp)$	-0.15821	+0.06404
$E_3^2(hh)$	+0.05703	0.0
$E_3^3(hh)$	+0.00300	+0.00562
$E_3^4(hh)$	+0.00595	+0.01187
$E_3(hh)$	+0.06597	+0.01749
$E_3^2$	-0.07361	+0.00866
$E_3^3$	+0.05878	+0.13020
$E_3^4$	+0.00595	+0.01187
$E_3$	-0.00888	+0.15072
$E_2 + E_3$	-0.46517	-0.41745
$E[2/1]$	-0.46535	-0.44905
$E(\text{upper bound})$	-0.41775	-0.39030

<sup>a</sup>Atomic units are used throughout this table.

TABLE V. Analysis of second-order energy for the perturbation expansion based on the model reference Hamiltonian at a nuclear separation of 2.89964 bohr.<sup>a</sup>

Chemical entity	Component of the second-order energy	Percentage of total second-order energy
sulphur core	-0.02336	5.1%
carbon core	-0.03015	6.6%
sulphur <i>L</i> shell	-0.09977	21.9%
valence shell	-0.25285	55.4%
total intra group	-0.40613	89.0%
sulphur core/carbon core	0.0	0.0%
sulphur core/sulphur <i>L</i> shell	-0.01197	2.6%
sulphur core/valence shell	-0.00075	0.2%
carbon core/sulphur <i>L</i> shell	-0.00001	0.02%
carbon core/valence shell	-0.00836	1.6%
sulphur <i>L</i> shell/valence shell	-0.02908	6.4%
total inter group	-0.05017	11.0%
total second-order energy	-0.45629	100.0%

<sup>a</sup>Atomic units are used throughout this table.

ciated with the sulfur *L* shell and 10 with the valence shell. These different groups are expected to be localized in different regions of space and we expect the components of the correlation energy to reflect this. Of the 231 pair interactions in CS only 75 are associated with the interaction of electrons in the same group.

An analysis of the second-order energy is given in Table V. 89% of the second-order energy is attributable to intragroup effects. The largest contribution comes from the valence electrons; however the largest contribution per pair arises from the tightly bound core electrons. The fact that the core correlation energy for the sulfur is less than that for the carbon atom is almost certainly a basis set effect. Of the intergroup components the sulfur *L* shell-valence shell interactions make the largest contribution. However, this is the sum of 80 pair interactions; the largest contribution per pair arises, as would be expected on simple physical grounds, from the interaction of the sulfur core with the sulfur *L* shell.

TABLE VI. Potential curves for the  $X^1\Sigma^+$  state of the carbon monosulfide molecule.<sup>a</sup>

<i>R</i>	$E_{\text{ref}}$	$E(3)$	$\bar{E}(3)$	$E[2/1]$	$\bar{E}[2/1]$
2.6	-435.32242	-435.78959	-435.75708	-435.78999	-435.77900
2.7	-435.33970	-435.80605	-435.76935	-435.80638	-435.79391
2.8	-435.34683	-435.81253	-435.77078	-435.81278	-435.79854
2.89964	-435.34627	-435.81145	-435.76372	-435.81162	-435.79532
3.0	-435.33991	-435.80434	-435.74987	-435.80474	-435.78609
3.1	-435.32930	-435.79362	-435.73074	-435.79366	-435.77244

<sup>a</sup>In atomic units.TABLE VII. Upper bounds to the potential energy curve for the  $X^1\Sigma^+$  state of the carbon monosulfide molecule.<sup>a</sup>

<i>R</i>	$E_{\text{u.b.}}$	$\bar{E}_{\text{u.b.}}$	$\gamma$	$\bar{\gamma}$
2.6	-435.74539	-435.72380	0.93181	0.72107
2.7	-435.76086	-435.73750	0.92706	0.71059
2.8	-435.76626	-435.74095	0.92163	0.69917
2.89964	-435.76403	-435.73657	0.91554	0.68694
3.0	-435.75599	-435.72624	0.90874	0.67385
3.1	-435.74370	-435.71157	0.90137	0.66011

<sup>a</sup>In atomic units.

## B. Calculated potential energy curves

### 1. Potential curves

In Table VI the calculated points on the potential energy curve for the  $X^1\Sigma^+$  state of the carbon monosulfide molecule are given. For that portion of the curve which has been studied we observe that the following inequalities are obeyed:

$$E(3) < \bar{E}(3) \quad (6)$$

$$E[2/1] < \bar{E}[2/1]. \quad (7)$$

The energies corresponding to the *model* perturbation expansion are consistently lower than those derived from the *shifted* expansion. Furthermore, it can be seen that the  $[2/1]$  Padé approximants are below the values obtained by simply truncating the corresponding perturbation expansions; that is,

$$E[2/1] < E(3) \quad (8)$$

$$\bar{E}[2/1] < \bar{E}(3). \quad (9)$$

In Table VII the calculated upper bounds to the potential energy curves are given. The inequality

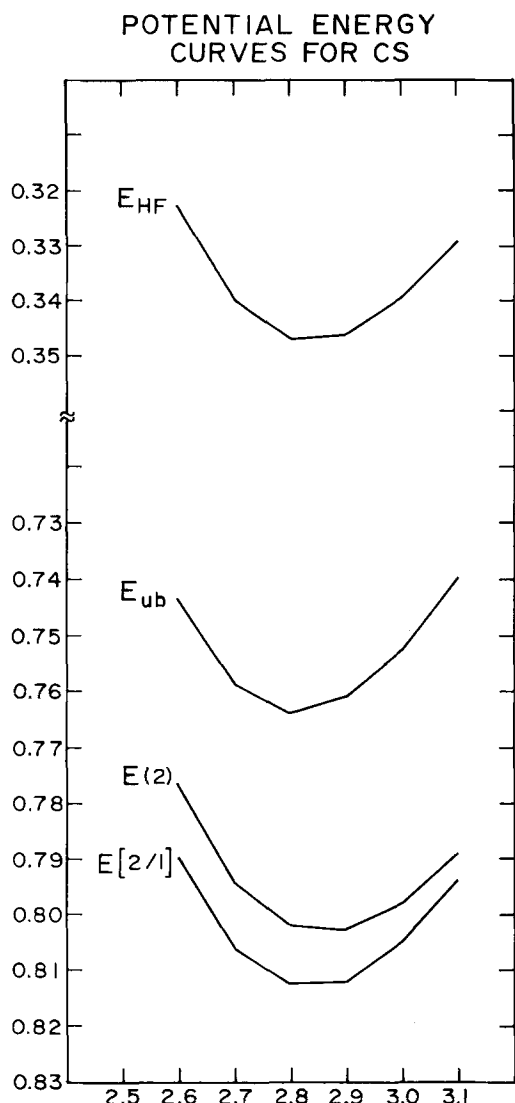
$$E_{\text{u.b.}} < \bar{E}_{\text{u.b.}} \quad (10)$$

indicates the superiority of the bounds derived from the *model* scheme. This observation is reinforced by the relation

$$\bar{\gamma} < \gamma < 1. \quad (11)$$

The wave function obtained from the *model* scheme provides a better representation of the true wave function than does the *shifted* function, and thus, when the parameter  $\gamma$  is optimized according to the variation theorem, the former yields a value closer to unity.

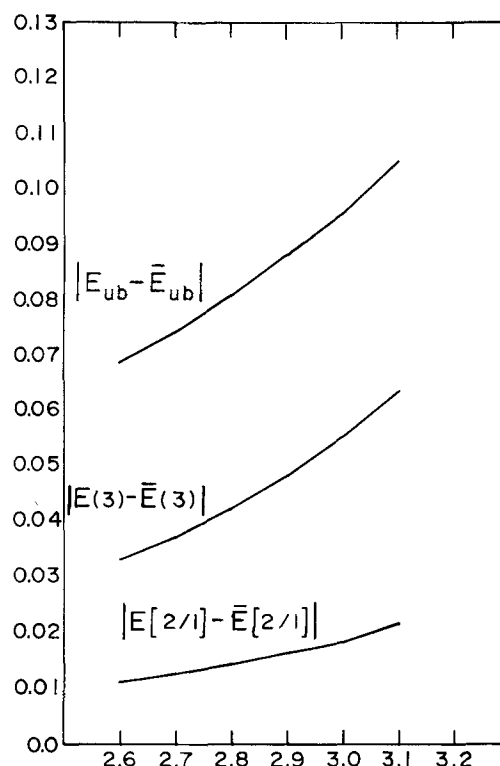
The potential energy curves resulting from the *model* perturbation expansion are sketched in Fig. 2 together

FIG. 2. Potential curves for the carbon monosulfide molecule.<sup>a</sup>

with the Hartree-Fock reference function.  $E[2/1]$  and  $E(3)$  are very close in this expansion and only the former is illustrated.

In Fig. 3 the difference between third-order quantities in the *model* and *shifted* expansions is shown as a function of nuclear separation. Since the converged energy is independent of the choice of reference operator, these differences give a measure of the extent to which convergence has been achieved. The differences plotted in Fig. 3 all increase as a function of nuclear separation reflecting the fact that the Hartree-Fock model does not describe molecular dissociation correctly. It can be seen that the  $[2/1]$  Padé approximants seem to provide the most uniform representation of the third-order energy.

The variation of the optimal variation parameters  $\gamma$  and  $\bar{\gamma}$  is shown in Fig. 4. Both  $\gamma$  and  $\bar{\gamma}$  decrease as the nuclear separation is increased again reflecting the fact that the Hartree-Fock reference function does not provide the description of molecular dissociation which is qualitatively correct. However, besides being closer

FIG. 3. Differences between *model* and *shifted* energies as a function of nuclear separation.

to unity than  $\bar{\gamma}$ , the value of  $\gamma$  changes less rapidly than  $\bar{\gamma}$  for the range of internuclear distances considered here.

## 2. Components of the calculated correlation energy

The second-order energy is necessarily negative for a neutral species and increases with nuclear separation since the Hartree-Fock model fails to provide a qualitatively correct description of molecular dissociation. The variation with nuclear geometry of the third-order energy and its components is shown in Fig. 5 for the

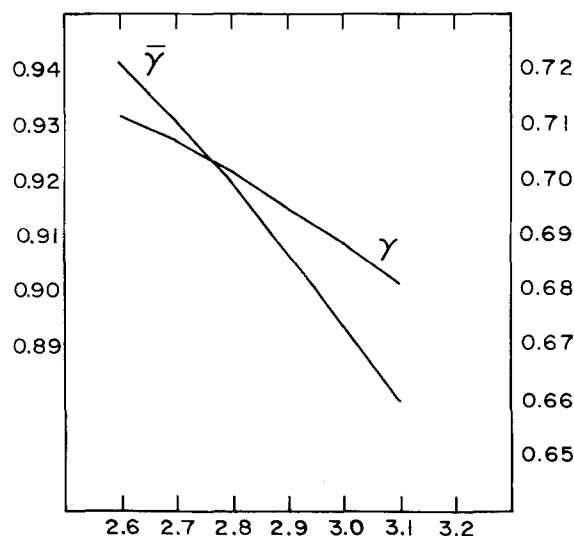
FIG. 4. Optimal parameters  $\gamma$  and  $\bar{\gamma}$  as a function of nuclear separation.

TABLE VIII. Calculated equilibrium internuclear separations and fundamental frequencies of vibration.<sup>a</sup>

Potential function	$r_e$			$\omega_e$		
	Model expansion	Shifted expansion	difference	Model expansion	Shifted expansion	difference
$E_{\text{ref}}$	1.503	1.503	0.000	1439	1439	0
$E(2)$	1.513	1.546	-0.033	1358	1198	160
$E(3)$	1.499	1.463	0.036	1444	1676	-232
$E_{\text{u.b.}}$	1.490	1.476	0.014	1486	1562	-76
$E[2/1]$	1.498	1.484	0.014	1446	1533	-87

<sup>a</sup>The calculated equilibrium nuclear separation,  $r_e$ , is given in Å; the calculated fundamental frequency of vibration,  $\omega_e$ , is given in  $\text{cm}^{-1}$ .

model perturbation expansion. All components of the third-order energy increase with increasing internuclear distance. We note that there is a considerable cancellation between these components and the total third-order energy is relatively small.

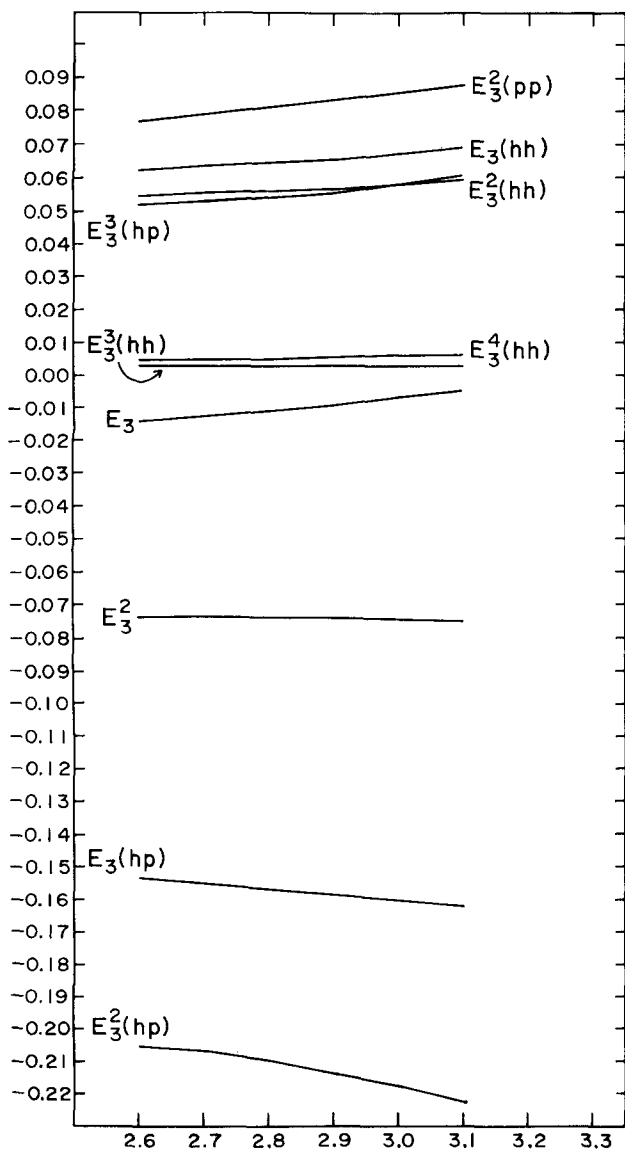


FIG. 5. Components of the third-order energy in the model expansion as a function of nuclear separation.

### 3. Spectroscopic constants

By fitting a polynomial to the calculated energy points, values of the equilibrium nuclear separation,  $r_e$ , and the fundamental frequency of vibration,  $\omega_e$ , were derived for each of the potential curves discussed above. The calculated values are given in Table VIII. Note the better agreement between values derived from the upper bounds and between those derived from the [2/1] Padé approximants for the *model* and *shifted* perturbation expansions. The calculated values given in Table VIII should be compared with those derived from experimental studies:  $r_e = 1.534_9$  Å,  $\omega_e = 1285.08$   $\text{cm}^{-1}$ .<sup>13</sup>

### C. Previous studies

The present calculation is compared with previous studies<sup>14-17</sup> in Table IX. In this table  $E_{\text{corr}}$  is the correlation correction with respect to the corresponding reference energy.

TABLE IX. A comparison of the present calculation with previous results.

Method	Reference	$-E_{\text{ref}}$	$-E_{\text{corr}}$	$-E_{\text{total}}$
Molecular orbital calculation	(a)	435.32969	...	...
Configuration interaction calculation	(b)	435.33037	0.075	435.40537
Configuration interaction calculation	(c)	435.3094	0.1468	435.4562
Configuration interaction calculation	(d)	435.3317	0.2591	435.5908
Diagrammatic perturbation theory, $E_{\text{u.b.}}$	(e)	435.34627	0.41776	435.76403
Diagrammatic perturbation theory, $E[2/1]$	(e)	435.34627	0.46535	435.81162

<sup>a</sup>W. G. Richards, Trans. Faraday Soc. **63**, 257 (1967).

<sup>b</sup>J. M. Robbe and J. Schamps, J. Chem. Phys. **65**, 5420 (1976),  $r = 2.8$  bohr.

<sup>c</sup>P. J. Bruna, W. E. Kramer, and K. Vasudevan, Chem. Phys. **9**, 91 (1975)  $r = 2.9$  bohr.

<sup>d</sup>S. Green, J. Chem. Phys. **54**, 827 (1971),  $r = 2.89964$  bohr.

<sup>e</sup>Present study.

The estimated nonrelativistic energy of the carbon monosulfide molecule at its equilibrium nuclear geometry is  $-436.22662$  hartree. This is  $0.415$  hartree below the present  $E[2/1]$  value and  $0.636$  hartree below the lowest reported value obtained by configuration interaction.

Robbe and Schamps<sup>15</sup> used the method of configuration interaction to obtain values of  $r_e$  ( $1.542$  Å) and  $\omega_e$  ( $1275$   $\text{cm}^{-1}$ ) which should be compared with the values given in Table VIII. These authors used a "double zeta" basis set of Slater functions: 18 of  $\sigma$  symmetry and 16 of  $\pi$  and  $\bar{\pi}$  symmetry. From their matrix Hartree-Fock calculation Robbe and Schamps obtained  $r_e = 1.511$  Å and  $\omega_e = 1430$   $\text{cm}^{-1}$ . The former is in closer agreement with the experimental value than the corresponding quantity in the present work. However, it is well known that the matrix Hartree-Fock model yields equilibrium nuclear separations for diatomic molecules which lie increasingly below the experimental value as the size of the basis set is increased. The fundamental frequency of vibration obtained from the matrix Hartree-Fock model by Robbe and Schamps is in good agreement with the value reported here. Upon performing a configuration interaction study, Robbe and Schamps obtained values of  $r_e$  and  $\omega_e$  which are in somewhat better agreement with experiment than those obtained in the present work. However, the basis set used in the configuration interaction study is more limited than that employed for the present perturbative study; in particular, the former does not contain any orbitals of  $\delta$  symmetry.

## V. CONCLUDING REMARKS

In the present study of the ground state of the carbon monosulfide molecule using diagrammatic perturbation theory, we have recovered almost 53% of the empirically estimated correlation energy. Although this is a considerable improvement on previous configuration

interaction studies, it cannot be considered to be of chemical accuracy. There are two truncation effects which determine the accuracy of this work. The first is the truncation of the perturbation series at third order. When the Hartree-Fock model is used to obtain a zero-order function, singly-, triply-, and quadruply-excited configurations first enter the perturbation series in fourth order. The second truncation effect arises from the use of a limited basis set. This is almost certainly the most important effect in the present work.

- <sup>1</sup>K. A. Brueckner, *Phys. Rev.* **100**, 36 (1955).
- <sup>2</sup>J. Goldstone, *Proc. R. Soc. London Ser. A* **239**, 267 (1957).
- <sup>3</sup>N. H. March, W. H. Young and S. Sampanthar, *The Many-Body Problem in Quantum Mechanics*, (Cambridge University, Cambridge, England, 1967).
- <sup>4</sup>H. P. Kelly, *Adv. Chem. Phys.* **14**, 129 (1969).
- <sup>5</sup>S. Wilson and D. M. Silver, *Phys. Rev. A* **14**, 1949 (1976).
- <sup>6</sup>S. Wilson and D. M. Silver, *J. Chem. Phys.* **66**, 5400 (1977); **67**, 1689 (1977).
- <sup>7</sup>D. M. Silver, *Comp. Phys. Comm.* (to be published).
- <sup>8</sup>S. Wilson, *Comp. Phys. Comm.* (to be published).
- <sup>9</sup>S. Wilson, D. M. Silver, and R. A. Farrell, *Proc. R. Soc. London Ser. A* **356**, 363 (1977).
- <sup>10</sup>A. D. McLean, in *Proceedings of the Conference on Potential Energy Surfaces in Chemistry*, edited by W. A. Lester, Jr., IBM Research Laboratory, 1971.
- <sup>11</sup>A. Veillard and E. Clementi, *J. Chem. Phys.* **49**, 2415 (1968).
- <sup>12</sup>*American Institute of Physics Handbook*, 3rd. ed. (McGraw-Hill, New York, 1972) Table 7g-1, p. 7-178.
- <sup>13</sup>L. M. Mills, *Specialist Periodical Reports-Theoretical Chemistry*, edited by R. N. Dixon (The Chemical Society, London, 1974), Vol. 1, p. 110.
- <sup>14</sup>W. G. Richards, *Trans. Faraday Soc.* **63**, 257 (1967).
- <sup>15</sup>J. M. Robbe and J. Schamps, *J. Chem. Phys.* **65**, 5420 (1976).
- <sup>16</sup>P. J. Bruna, W. E. Kramer, and K. Vasudevan, *Chem. Phys.* **9**, 91 (1975).
- <sup>17</sup>S. Green, *J. Chem. Phys.* **54**, 827 (1971).