

A COMPLETE FOURTH-ORDER MANY-BODY PERTURBATION-THEORY STUDY OF THE GROUND STATE OF SiS*

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ABSTRACT

A comparison of different MBPT calculations of the ground state spectroscopic constants of SiS is made. The calculations are made up to the complete fourth-order MBPT level with inclusion of all single, double, triple and quadruple substitutions utilizing double-zeta-plus polarization basis sets. The MBPT(3) results give the best agreement with the experimental data. The results of the higher MBPT(4) level give a too long internuclear distance and a too short vibration frequency as compared to experiment and indicate the importance of even higher-order contributions to the correlation energy. They very good results of the MBPT(3) calculations indicate mutual cancellation of different higher-order terms. These aspects are discussed together with possible sources of inaccuracies.

INTRODUCTION

The total energy of an atomic or molecular system may conveniently be divided into two parts [1]. One is the self-consistent-field (SCF) energy which is obtained from a wave function consisting of a single determinant and the other is the correlation energy. Although the SCF method most often gives more than 99% of the total nonrelativistic energy of the system it is the remaining approximately 1% that is required for "chemical accuracy". The challenge of ab initio quantum mechanical calculations is to obtain in a systematic way the correlation contribution to the total energy and consequently to describe accurately chemical and physical processes.

Two methods have dominated the post-SCF calculations: Configuration Interaction (CI) [2, 3] and Many-Body Perturbation Theory (MBPT) [4-7]. Due to the linked-cluster theorem [4-7, 8-9] the MBPT approach provides a highly systematic scheme to obtain the correlation energy. Incomplete CI, as opposed to full CI, is not size-extensive [6] and this is the most clear disadvantage of CI over MBPT. As full CI calculations are not feasible to most molecular systems we do not hope to retrieve the size-extensivity property from CI calculations. The CI energy thus, in general, has the wrong dependence on the "size" of the system. Whether this is a real problem for chemical/physical descriptions is a system- and property-dependent question. On the other hand, MBPT by virtue of the linked cluster theorem guarantees size-extensivity regardless of possible truncations. Size-extensivity is a natural consequence of models based upon the linked diagram theorem of Brueckner and Goldstone [8, 9].

In this paper we perform MBPT calculations of the potential energy curve of SiS. One of the main purposes of the present study is to investigate the performance of different MBPT schemes in calculating the interacting energy of this important system and the accuracy of the related ground state spectroscopic constants.

SiS is the second row analog of CO and has been of interest to spectroscopists since 1938 [10-16]. Recently, its possible importance in the interstellar space has been discussed [17], particularly in the protonated forms [17, 18]. More recently, analyses of several rotational bands belonging to the $E^1\Sigma^+ - X^1\Sigma^+$ system of SiS have been made [16]. By combining the band origin data with those of previous investigations both vibrational and rotational constants for the ground $X^1\Sigma^+$ state of SiS were accurately obtained [16]. The present investigation theoretically calculates these constants by utilizing a complete fourth-order MBPT calculation with inclusion of all single, double, triple and quadruple substitutions with a double-zeta plus polarization basis set; a scheme by all present standards, considered of good accuracy [19]. No attempt is made to discuss the closely related method of coupled-cluster [6] where promising progresses are underway.

THEORY

A detailed discussion of MBPT and its relationship to CI methods has been published [6, 20, 21]. This section will be limited to the information and notation of the different models to be used.

In MBPT, the energy is given by the linked diagram expansion [5, 9].

$$\Delta E = E - E_0 = E_1 + E_{\text{corr}}$$

$$= \sum_{n=0}^{\infty} \langle \Phi_0 | V | (E_0 - H_0)^{-1} V |^n | \Phi_0 \rangle_L$$

The function Φ_0 is the usual Hartree-Fock (or, in a finite basis set, SCF) result for a nondegenerate ground state, with H_0 the sum of one-electron Fock operators and E_0 the sum of SCF orbital energies, so that $E_{\text{SCF}} = E_0 + E_1$. The perturbation is $V = H - H_0$, where H is the usual electrostatic Hamiltonian, and the subscript L indicates the limitation to linked diagrams.

The correlation correction, E_{corr} , can be expanded into the correlation perturbation series,

$$E_{\text{corr}} = \sum_{k=2}^{\infty} E_k$$

Each k -th order correlation energy, E_k , can then be partitioned into a finite number of terms corresponding to different intermediate states which contribute to the reduced resolvent and can be generated from the given single determinant SCF reference function. Hence, the n -th order correction can be written in general as

$$E_n = \Delta E_{\text{corr}}^{\text{MBPT}}(n) = E_n^{\text{S}} + E_n^{\text{D}} + E_n^{\text{T}} + E_n^{\text{Q}} + \dots$$

where S, D, T, Q, ... refer to singly, doubly, triply, quadruply, ... substituted intermediate states in the reference SCF determinant, respectively, and MBPT means that all terms satisfy the linked-cluster theorem. The complete fourth-order MBPT approach is employed in the present study but some approximate and lower-order schemes will also be discussed.

We now summarize the approximations and formulae which will be referred to in the present paper [22–24].

MBPT(2):

$$\Delta E_{\text{corr}}^{\text{MBPT}}(2) = E_2^{\text{D}},$$

where only doubly substituted intermediates contribute to second-order.

MBPT(3):

$$\Delta E_{\text{corr}}^{\text{MBPT}}(3) = E_3^{\text{D}}$$

where again only doubly substituted intermediates contribute to third-order.

$$\text{MBPT}(3) = \text{MBPT}(2) + \Delta E_{\text{corr}}^{\text{MBPT}}(3) = E_2^{\text{D}} + E_3^{\text{D}}$$

MBPT(4):

$$\Delta E_{\text{corr}}^{\text{MBPT}}(4) = E_4^{\text{S}} + E_4^{\text{D}} + E_4^{\text{T}} + E_4^{\text{Q}}$$

where it is to be noted that singly, doubly, triply and quadruply substituted intermediates contribute to fourth-order.

$$\begin{aligned} \text{MBPT}(4) &= \text{MBPT}(3) + \Delta E_{\text{corr}}^{\text{MBPT}}(4) \\ &= E_2^{\text{D}} + E_3^{\text{D}} + E_4^{\text{S}} + E_4^{\text{D}} + E_4^{\text{T}} + E_4^{\text{Q}} \end{aligned}$$

For the sake of comparison of the complete and incomplete fourth-order results it is worth while to define some approximate fourth-order energies:

$$\text{SDQ-MBPT}(4) = E_2^{\text{D}} + E_3^{\text{D}} + E_4^{\text{S}} + E_4^{\text{D}} + E_4^{\text{Q}}$$

$$\text{SD-MBPT}(4) = E_2^{\text{D}} + E_3^{\text{D}} + E_4^{\text{S}} + E_{4\text{d}}^{\text{D}}$$

The SDQ-MBPT(4) incomplete fourth-order amounts to neglecting the contribution of triple excitations in the reference SCF determinant, which are usually the most time-consuming ones to compute. The SD-MBPT(4) neglects both the triply and quadruply intermediates. To maintain size-extensivity in this approximation only the disjoint $E_{4\text{d}}^{\text{D}}$ part of $E_4^{\text{D}} = E_{4\text{d}}^{\text{D}} + E_{4\text{r}}^{\text{D}}$ is included, i.e. the fourth-order $E_{4\text{r}}^{\text{D}}$ renormalization term is excluded [20].

Otherwise, one has what is termed SD-RSPT(4), the fourth-order Rayleigh-Schrödinger perturbation theory approximation which suffers from the contribution due to unlinked clusters [20]. This SD-MBPT(4) scheme can be derived as an approximation to a variational treatment of the total correlation energy [25]. In our study the solely incomplete treatment considered is the SDQ-MBPT(4). The essential reason is that the results of incomplete fourth-order MBPT calculations appear to be more sensitive to the choice of basis set than those of the complete MBPT(4) treatment. As a consequence it turns out that the contribution of triply substituted intermediates may become quite significant [19]. We thus separate out this contribution from the SDQ-MBPT(4) results to verify the explicit role of the triply substituted intermediate states in our calculations.

Extending the MBPT treatment to higher order presents a formidable computational task [26]. At present this is possible only under two limitations: i) the use of a poor basis [26] set leading to a very poor approximation to the one-particle states or ii) the incomplete treatment of the higher-order terms. In the first case the increase in accuracy is questionable because using poor basis sets leads to meaningless calculation of the correlation energy as a great part of it may turn out to be just improvement of the SCF energy itself. In the second case we would have incomplete contribution to higher-order (fifth- or sixth-order) terms but those terms neglected may well destroy the delicate balance between the different diagrammatic contributions [20, 27]. Under these circumstances it is believed that the best MBPT calculation possible at present is the complete fourth-order with inclusion of all single, double, triple and quadruple substitutions. This is the present "state-of-the-art" in MBPT calculations. Any further improvement, must be carried out either by increasing the basis set size (i.e. the number of one-particle states) or by means of complete fifth- or higher-order approaches, or both. These aspects will be discussed later on in relation to our present calculations on SiS. There is little chance at present to perform complete fifth- or higher-order calculations for this system with a reasonable basis set. In the next section we present the basis set utilized in our calculations along with the computational details.

METHOD AND CALCULATION

The calculations were performed using the GAUSSIAN-82 program package [28]. The program calculates ground state total energy in the SCF approximation and utilizes the set of optimized molecular orbitals to obtain the correlation energy by using second-, third-, and fourth-order MBPT in the Moller-Plesset approach [29]. In all calculations we have utilized the frozen core approximation thus neglecting the contributions of inner shell orbitals. By virtue of the linked-cluster theorem the MBPT approach

see that the fourth-order contribution $\Delta E_{\text{CORR}}^{(4)}$ is larger than the third order $\Delta E_{\text{CORR}}^{(3)}$ one. Thus, the higher-order corrections may not be negligible. Therefore, the very good results of the MBPT(3) scheme may be considered as fortuitous. According to these calculations their agreement with the experimental data follows from the mutual cancellation of different higher-order terms. The system-independence of this favourable cancellation is of course questionable and may not be used in favour of a wide spread belief on the general accuracy of the MBPT(3) level of calculation. Interesting enough, this is the same situation occurring for the analog CO [19], even for large basis set calculations. In this case also the MBPT(3) scheme gives the best result and similarly indicates that higher-order contributions should be of importance. The data of Table III also show that the second order contribution $\Delta E_{\text{CORR}}^{(2)}$ amounts to ~87% of the total calculated correlation energy. It is well known that the $\Delta E_{\text{CORR}}^{\text{MBPT}}(2)$ is generally the largest term in the MBPT expansion and very often can give more than 80% of the total correlation energy [21]. Yet, in the present case, it is not able of giving more than reasonable results for the spectroscopic constants. The R_e and ω_e values calculated at the MBPT(2) level are too high by 0.015 Å and 22 cm⁻¹, respectively. Analysing now the contribution to fourth-order of the triply substituted intermediates E_4^{T} we see from Table III that it is as important as the third-order contribution and is almost entirely responsible for the total fourth-order $\Delta E_{\text{CORR}}^{(4)}$ contribution. As remarked before, the results of complete MBPT(4) are less sensitive to the choice of basis set than are those of the incomplete fourth-order and this tends to give particular importance to the triply substituted intermediates [19]. This contribution though small is quite significant. Its distance dependence considerably affects the shape of the calculated potential energy curve as it can be seen in Table II by comparing the SDQ-MBPT(4) and MBPT(4) results. The inclusion of E_4^{T} increases the bond distance by 0.022 Å and decreases the vibrational frequency by 36 cm⁻¹. This is indeed a dramatic change and illustrates the importance of considering complete MBPT schemes. For comparison, the change in the calculated value of R_e , by the neglect of the E_4^{T} term alone, is close to the second-order MBPT(2) change, compared to the SCF value, even though E_4^{T} contributes around 5% to the total calculated correlation energy, compared to the contribution of 87% of the MBPT(2).

The calculations performed by Berthier et al. [17] also give too long bond-distances after inclusion of correlation corrections via a CI procedure. As discussed in the present paper, it seems that good agreement for the spectroscopic constants of SiS with the experimental data requires a considerable amount of correlation energy and any low-order procedure may give only fortuitous agreement.

SUMMARY AND CONCLUSIONS

In the present paper we have reported a series of different MBPT calculations of the potential energy curve for the ground state of SiS. The method used in this paper provides a highly systematic determination of the correlation energy contribution. Comparison with the experimental data for the spectroscopic constants calculated in this paper is, of course, by itself the best way to check the accuracy of the calculation. To establish the possible sources of theoretical errors three points are considered of importance.

First, both the SCF and MBPT calculations are made by using the expansion of single particle states into a truncated set of basis functions. Within this approach the calculation of interaction energies brings about what is termed the basis set super-position error [31-35]. Each subsystem uses the functions of the basis set of the other subsystem to improve its own energy. The calculated energies are thus contaminated by the artificial lowering of energies of the interacting atoms which arises from combining the atomic basis sets into the molecule basis set. One possible way to estimate the basis set superposition error on both the SCF and MBPT interaction energies is the counterpoise method [35]. No attempt has been made to correct for this deficiency. The basic reason being that the correction in the counterpoise method requires the calculation of the energies of the two atoms with the molecule basis set at a given geometry. However, the present subsystems are open shell atoms and we can not handle MBPT calculations for this case [6, 7, 21]. The importance of the basis set superposition error can be minimized by using sufficiently large basis sets. A second source of theoretical error is the interpolation procedure for obtaining the spectroscopic constants. In our investigation this has been minimized by a great number of calculations around the corresponding minima. Still, different procedures may give different results. Essentially, two different schemes have been adopted: polynomial interpolation and least square fit to the Fues curve $E = C_0 + C_1 R^{-1} + C_2 R^{-2}$. In general, they gave the same results but in one case of a small discrepancy (ω_e for MBPT (2)) we have favoured the polynomial fit around the minima. However, none of the conclusions of this paper depend on this particular choice. Finally, in discussing reliability of MBPT calculations it is important to analyse the perturbation series. As discussed in the previous section, the fourth-order contribution $\Delta E_{\text{CORR}}^{(4)}$ is larger than the third order $\Delta E_{\text{CORR}}^{(3)}$ one. This is indicative that the fifth-order contribution may be of great importance. However, the calculation of higher order terms presents formidable computational difficulties if it is to be carried out with extensive basis sets. The use of poor basis sets or the incomplete treatment of higher order contribution do not seem to be justified. At the present computational standards the only possibility we feel viable to improve our results is by extending the basis set size. A judicious extension may slightly improve the results [36]. Other than that, one may easily achieve the position where there will be little chance for the calculations to be performed in a system like SiS with the present computational resources.

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TABLE II

Comparison of the different MBPT calculations of the ground state spectroscopic constants of SiS with the experimental data (see text for notation).

	SCF	MBPT(2)	MBPT(3)	SDQ-MBPT(4)	MBPT(4)	Experiment	CI ^(b)
R (Å)	1.914	1.944	1.931	1.939	1.961	1.929 ^(a)	1.939
ω_e (cm ⁻¹)	891	771	738	704	668	749.5	795
B_e (cm ⁻¹)	0.308	0.299	0.303	0.300	0.294	0.303528	0.300

a) Value obtained from the experimental B_e result assuming $^{28}\text{Si}^{32}\text{S}$. Conversion factors are: $1a_0 = 0.529167\text{Å}$; $1\text{h} = 219475.86\text{cm}^{-1}$

b) From ref. 37.

TABLE III

Order-by-order contributions to the complete fourth-order MBPT calculation of the ground state energy of SiS (see text for notation).^{a)}

	R = 1.929 Å	R = 1.96 Å
SCF	-686.47481	-686.47371
$\Delta E_{\text{corr}}^{\text{MBPT}}(2)$	-0.19438	-0.19550
$\Delta E_{\text{corr}}^{\text{MBPT}}(3)$	-0.01330	-0.01270
E_T^4	-0.01126	-0.01190
$\Delta E_{\text{corr}}^{\text{MBPT}}(4)$	-0.01529	-0.01635
MBPT(2)	-686.66919	-686.66921
MBPT(3)	-686.68249	-686.68191
SDQ-MBPT(4)	-686.68652	-686.68636
MBPT(4)	-686.69778	-686.69826

a) The two internuclear distances correspond to the experimental data and optimized MBPT(4) results. All energies in atomic units.

does not involve disjoint diagrammatic contributions to the energy, and thus, is size-extensive, independent of possible approximations. Potential energy curves and spectroscopic constants for SiS were thus calculated in five schemes, namely, SCF, MBPT(2), MBPT(3), MBPT(4) and the incomplete SDQ-MBPT(4).

For both atoms the original basis set consisting of (12s 9p) contracted by McLean and Chandler [30] to [6s 4p] was augmented with a set of polarization d functions ($\alpha_d^{\text{Si}} = 0.8$ and $\alpha_d^{\text{S}} = 0.54$). The final basis set therefore consists of the primitive (12s 9p 1d) contracted to [6s 4p 1d] with a total of 46 CGTO's. In the ground state 15 molecular orbitals are doubly occupied and 31 are virtuals. For the calculation of the correlation energy all virtuals are considered for the excited intermediates and out of the 15 occupied, 10 are the 1s, 2s and 2p core orbitals that are excluded in the generation of the excited intermediate states.

At the experimental distance of 1.929 Å the calculated SCF total energy is -686.47481 hartree. The ground state molecular orbital configuration and corresponding energies are given in Table I.

TABLE I

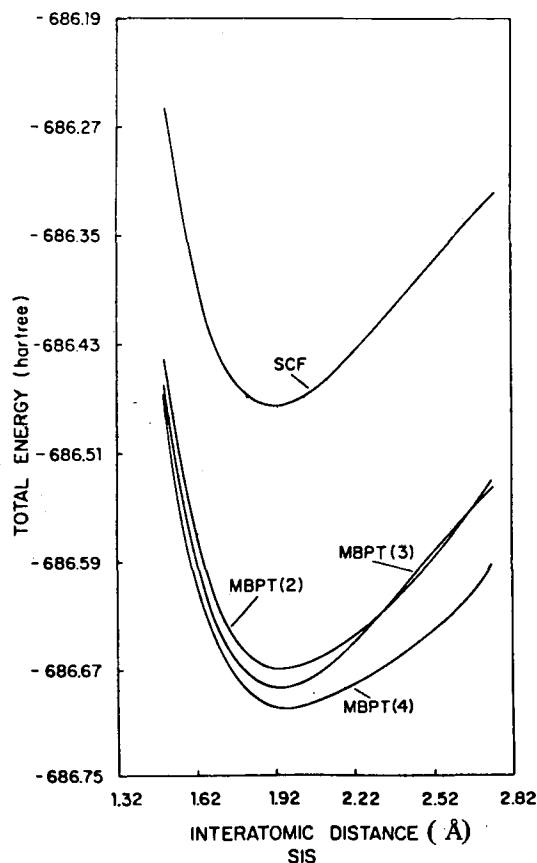
Calculated molecular orbital configuration and energies for the SCF calculation at the experimental internuclear distance of $R = 1.929 \text{ \AA}$. All energies in atomic units.

m.o	σ	π
$-\epsilon_i$	91.94301	6.62728
	68.84337	4.29032
	8.94780	0.38917
	6.62947	
	6.18928	
	4.29058	
	0.95268	
	0.57883	
	0.39305	

$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 6\sigma^2 2\pi^4 7\sigma^2 8\sigma^2 9\sigma^2 3\pi^4$

RESULTS AND DISCUSSION

The total energies of SiS at different internuclear distances were obtained at the SCF, MBPT(2), MBPT(3), SDQ-MBPT(4) and MBPT(4) levels of calculations. The potential curves obtained are shown in Figure 1. For clarity of the picture the incomplete SDQ-MBPT(4) is not shown in the figure. In all cases the MBPT(n) curves have a fairly regular shape. For large internuclear distances convergence problems at the SCF level precluded the calculation of the entire potential energy curves. However, the spectroscopic constants are essentially obtained around the corresponding minima and therefore that is of little importance. Furthermore, it is well known that the MBPT treatment fails down in the case of near degeneracies [6, 21] and this is very common when breaking chemical bonds. Hence, for systems whose dissociation limit is not properly accounted



Calculated potential energy curves for the ground state of SiS from complete MBPT(n) schemes.

for by the SCF scheme, the study must be limited to a narrow range of internuclear separations. Our calculations are made between $1.50 \text{ \AA} < R < 2.74 \text{ \AA}$ which for all cases considered encloses the region between the classical turning points for the first few vibrational levels.

The calculated spectroscopic constants are summarized in Table II. The SCF value of 1.914 Å for the bond distance is too short compared to the experimental result by 0.015 Å. Upon inclusion of correlation contribution one obtains the expected trend of increasing bond distances. In MBPT(2) the distance becomes too large compared to experiment with a total increase compared to the SCF result of 0.030 Å. The best result compared to experiment is obtained at the MBPT(3) level. This is also valid for the vibrational frequency. Both the SDQ-MBPT(4) and the complete fourth-order MBPT(4) give bond distances that are too long. Using more sophisticated approaches give too long values for the bond distance and too low harmonic frequencies. For comparison, Table II. also shows that the CI calculations gives too high values for both R_e and ω_e as well as MBPT(2). The failure of the fourth-order schemes to provide a quantitative agreement for R_e and ω_e with the experimental data appears to indicate that going beyond the fourth-order scheme may be necessary. This is further supported by the inspection of the data of Table III. In this table we show the order-by-order contribution to the total computed correlation energy at two different internuclear separations, corresponding to the experimental data and the result of the MBPT(4) calculations. In both cases we

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