Effective Valence Shell Hamiltonian Calculations on Spin-Orbit Coupling of SiH, SiH^+, and SiH^{2+}

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Recently the *ab initio* effective valence shell Hamiltonian method H^v has been extended to treat spin-orbit coupling in atoms or molecules. The quasidegenerate many-body perturbation theory based H^v method has an advantage of determining the spin-orbit coupling energies of all valence states for both the neutral species and its ions with a similar accuracy from a single computation of the effective spin-orbit coupling operator. The new spin-orbit H^v method is applied to calculating the fine structure splittings of the valence states of SiH, SiH^+, and SiH^{2+} not only to assess the accuracy of the method but also to investigate the spin-orbit interaction of highly excited states of SiH species. The computed spin-orbit splittings for ground states are in good agreement with experiment and the few available *ab initio* computations. The ordering of fine structure levels of the bound and quasi-bound spin-orbit coupled valence states of SiH and its ions, for which neither experiment nor theory is available, is predicted.

Key Words : Effective Hamiltonian, Spin-orbit coupling, SiH

Introduction

The computation of the spin-orbit coupling, *i.e*., the fine structure of molecules, is relevant to an understanding of their electronic spectra, non-radiative decays, dissociation mechanism and fine structure populations in photodissociations, and more. This relativistic effect can, in principle, be calculated directly by using the four-component Dirac theory, but it remains a formidable task to include the effects of electron correlation into relativistic spin-orbit coupling calculations. A widely used non-relativistic approach appends the approximate Breit-Pauli spin-orbit coupling operator to the non-relativistic Hamiltonian, so the spin-orbit coupling operator is treated as a perturbation.[1,2] This approximation is found to be reasonable for systems where the spin-orbit interaction is weak or moderate.

The majority of previous computations of spin-orbit couplings are based on the variation method, *i.e*., on configuration interaction (CI) calculations. To include electron correlation properly, large CI calculations must be performed, and the resulting CI wave functions are then used to calculate the spin-orbit couplings by directly evaluating the expectation values of the Breit-Pauli operator. A serious drawback of this method arises when computing off-diagonal spin-orbit couplings between different electronic states because the CI wave functions for different states generally involve different sets of molecular orbitals. On the other hand, there have been some perturbation approaches for spin-orbit coupling.[3] Particularly Fedorov and Finley reported the spin-orbit coupled term values for selected atoms using their own spin-orbit multireference multistate perturbation theory.[4]

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Recently Sun and Freed proposed another perturbation theory for spin-orbit coupling by extending the well known effective valence shell Hamiltonian (H^v) method which is based on quasidegenerate many-body perturbation theory.[5] The efficiency and accuracy of the non-relativistic H^v method has already been tested and demonstrated with numerous examples, and several studies of the convergence properties explain why these successes have been achieved.[6-10] The new effective valence shell spin-orbit Hamiltonian is defined by the projection of total Hamiltonian, which is a sum of the non-relativistic Hamiltonian (H) and the Breit-Pauli spin-orbit coupling operator (A), onto the prechosen valence space. Therefore the exact Breit-Pauli spin-orbit coupling operator is also projected onto the valence space, and, consequently, all diagonal and off-diagonal valence space matrix elements of the effective spin-orbit coupling operator (A^v) are computed. In this way, Sun and Freed achieved that the influence of electron correlation is incorporated perturbatively into the effective spin-orbit coupling operator A^v, and off-diagonal spin-orbit coupling matrix elements automatically emerge along with the diagonal expectation values. In principle, the A^v perturbation expansion is identical to the multireference, multistate perturbation treatment of Fedorov and Finley,[4] but a large difference between the two methods arises because the effective valence shell Hamiltonian H^v (and A^v) that is unambiguously defined within the full subspace, and the matrix elements of H^v (and A^v) can be consistently used to describe any state within the valence space.

The use of H^v (and A^v) has the following advantages: Once the matrix elements of H^v and A^v are evaluated, all the spin-orbit coupled valence state energies for the low-lying states of interest are generated with balanced accuracies. This A^v perturbation method converges in a practical sense provided the orbital energies of core, valence and excited orbitals are

well separated.[10] The A^v effective operator is independent of the number of valence electrons, which implies that the states of the neutral and its ions are simultaneously calculated with one set of A^v matrix elements. The method is size-consistent, and the forced degeneracy approach used eliminates almost all problems from intruder states that plague many other multireference perturbative methods.

It is interesting to see how well the new effective valence shell spin-orbit Hamiltonian method produces the spin-orbit coupling energies of SiH species. The SiH is one of interesting systems in photodissociation study where spin-orbit coupling plays a crucial role in determining the product (Si or H) distributions.[12] In the present computations, the valence state energies are calculated through second order H^v in the perturbation due to electron correlation, and the expectation values of the spin-orbit coupling operator is corrected through first order A^v in electron correlation. Due to the characteristics of H^v method, all valence states of SiH^+ and SiH^{2+} ions as well as the neutral SiH are simultaneously investigated. The theory behind the H^v and A^v formalism is summarized in the next section and computational procedure and results are provided in the following sections.

Effective Valence Shell Spin-Orbit Hamiltonian

The non-relativistic effective valence shell Hamiltonian H^v is obtained by projecting the full Hamiltonian onto a valence space that is spanned by a pre-chosen set of valence orbitals. The projection can be accomplished with the aid of quasi-degenerate many-body perturbation theory. Perturbation theory decomposes the molecular electronic (non-relativistic) Hamiltonian H into a zeroth order part H_0 and a perturbation V,

$$H = H_0 + \mathrm{V} \tag{1}$$

Quasidegenerate many-body perturbation theory (QDMBPT) transforms the full Schrödinger equation,

$$H\Psi_i = E_i\Psi_i \tag{2}$$

into the P space effective valence shell Schrödinger equation,

$$H^v\Psi_i^v = E_i\Psi_i^v \tag{3}$$

for the projection $\Psi_i^v = P\Psi_i$ of the exact wave functions onto the valence space, where the E_i are the exact eigenvalues of full Hamiltonian H, *i.e.*,

$$E_i = \langle \Psi_i|H|\Psi_i\rangle = \langle \Psi_i^v|H^v|\Psi_i^v\rangle \tag{4}$$

The Hermitian form of H^v is

$$H^v = PHP + \frac{1}{2}\sum_{\Lambda,\Lambda'} \{P(\Lambda)VQ[E_\Lambda - H_0]^{-1}QVP(\Lambda') + h.c.\} + \cdots \tag{5}$$

where *h.c.* designates the Hermitian conjugate of the preceding term and $P(\Lambda) = \sum_\Lambda |\Lambda><\Lambda|$ designates the projector onto the zeroth valence space function $|\Lambda>$, and $P + Q = 1$. In applications of the method, the space spanned by P, the valence space, consists configurations with all core spin-orbitals doubly occupied, excited spin-orbitals vacant, and all possible occupancies of the valence spin-orbitals.

To compute a molecular property that is represented by the Hermitian operator A, the above theory may be applied using the perturbed Hamiltonian $H_{total} = H + A$, where H is the non-relativistic Hamiltonian as in the above equations. Since we desire only the diagonal and off-diagonal matrix elements of the operator A between the exact normalized wave functions Ψ_i, these matrix elements $<\Psi_i | A | \Psi_j>$ may be transformed using QDMBPT into the matrix elements of an effective valence shell operator A^v between the orthonormal valence space eigenfunctions Ψ_i^v of the H^v operator,

$$<\Psi_i | A | \Psi_j> = <\Psi_i^v | A^v | \Psi_j^v>. \tag{6}$$

Again specifying that A^v be Hermitian and independent of the state Ψ_i leads to the lowest nontrivial first order perturbative expansion,

$$A^v = PAP + \frac{1}{2}\sum_{\Lambda,\Lambda'} \{P(\Lambda)VQ[E_\Lambda - H_0]^{-1}QAP(\Lambda') + P(\Lambda)AQ[E_\Lambda - H_0]^{-1}QVP(\Lambda') + h.c.\}, \tag{7}$$

where *h.c.* designates the Hermitian conjugate of the preceding two terms. The first order approximation to the effective operator A^v in Eq. (7) is sufficiently accurate when A is small. Note that the matrix elements of the leading contribution PAP in Eq. (7) corresponds to the matrix A within the P valence space, while the remainder include "correlation" corrections involving configurations in the orthogonal Q space.

The energy independent form of A^v can be decomposed as

$$A^v = A_c^v + \sum_i^{N_v} A_i^v + \frac{1}{2}\sum_i^{N_v}\sum_{j(\neq i)}^{N_v} A_{ij}^v + \frac{1}{3!}\sum_i^{N_v}\sum_{j(\neq i)}^{N_v}\sum_{k(\neq i\neq j)}^{N_v} A_{ijk}^v + \cdots \tag{8}$$

where N_v is the number of valence electrons, A_c^v is the constant contribution from the core, A_i^v is a one-electron effective operator with matrix elements $<v | A_i^v | v'>$ in the valence orbital basis set $\{v\}$, *etc*. For the spin-orbit operator, the first order expansion produces the effective spin-orbit operator A^v with up to three-electron effective operators A_{ijk}^v. The projected H^v (or A^v) is called the effective valence shell Hamiltonian (or A^v operator).

The Breit-Pauli spin-orbit coupling operator (H_{so}) is substituted as the perturbation operator A, *i.e.*,

$$A \equiv H_{so} = \frac{\alpha^2}{2}\sum_I\sum_N \frac{Z_N}{r_{IN}^3}[\overrightarrow{r_{IN}}\times\vec{p}_I]\cdot\vec{s}_I - \frac{\alpha^2}{2}\sum_I\sum_{J(\neq I)}\frac{1}{r_{IJ}^3}[\overrightarrow{r_{IJ}}\times\vec{p}_I]\cdot[\vec{s}_I + \overrightarrow{2s_J}] \tag{9}$$

where the indices *I, J* designate the electrons, *N* denotes the nuclei, and α is the fine-structure constant. $\vec{s}_I$ is the spin operator for electron *I*, $\overrightarrow{r_{IN}}$ is the position vector of electron *I* from the nucleus *N*, $\vec{p}_I$ is the momentum vector of electron *I*, $\overrightarrow{r_{IJ}}$ is the relative position vector of electron *I* with respect to electron *J*, r_{IN} is the distance between electron *I* and nucleus *N*, r_{IJ} is the distance between electron *I* and *J*, Z_N is the nuclear charge of nucleus *N*. The Breit-Pauli spin-orbit coupling operator is appropriate for describing systems with moderate or weak spin-orbit coupling.

The expectation values of H^v from (4) and A^v from (6) may be evaluated as a first approximation using the matrix elements of H^v and A^v between the eigenfunctions Ψ_i^v of H^v. An improved representation is generated when both matrices are added together to form the spin-orbit perturbed valence space configuration interaction (CI) matrix between the valence states. The diagonalization of the spin-orbit perturbed CI matrix yields the spin-orbit coupled energies of all valence states simultaneously from a single computation of H^v and A^v. The algebraic expressions for the A^v matrix elements in (8) are provided in the article by Sun and Freed.[5]

Computations and Results

The evaluation of the spin-orbit coupling energy using the A^v formalism proceeds as follows: i) Choose a basis set. For convenience, real atomic radial functions are used. Calculate the necessary integrals between basis functions. We used the GAMESS package[13] to calculate the orbital angular momentum ($\hat{l} = \hat{r} \times \hat{p}$) integrals over real atomic functions. ii) Self consistent-field (SCF) calculations are performed for the ground electronic state to generate an initial set of molecular orbitals and orbital energies. The SCF molecular orbitals are divided into three groups, the core, valence and excited orbitals. The collection of valence orbitals forms the valence space. iii) The non-relativistic Hamiltonian and spin-orbit coupling integrals in the atomic orbital basis are transformed to those over molecular spin-orbitals. iv) Evaluate the matrix elements of the effective Hamiltonian operator H^v and the effective spin-orbit operator A^v. v) Construct the spin-orbit symmetry adopted configuration state functions (linear combinations of Slater determinants corresponding to $|\Lambda\Sigma\Omega>$ eigenfunctions for a linear molecule like SiH) within the valence space. vi) Set up the valence space CI matrices for H^v+A^v using the second order approximation of Eq. (5) for H^v and the first order approximation of Eq. (7) for A^v. vii) The valence CI matrix is a real symmetric matrix because the matrix elements of A^v are evaluated in a spin-orbital basis and because the full spin-orbit symmetrized configuration state functions are used. Finally, diagonalize the CI matrix to generate the eigenvalues which are the spin-orbit perturbed energies of the valence states.

The basis set utilized is the correlation consistent aug-cc-pVTZ basis, *e.g.*, for Si the primitive (15*s*,9*p*,2*d*,1*f*) Gaussian functions are contracted to [5*s*,4*p*,2*d*,1*f*] with diffuse (1*s*,1*p*,1*d*,1*f*) functions added and for H (5*s*,2*p*,1*d*) → [3*s*,2*p*,1*d*](1*s*,1*p*,1*d*).[14-17] The core comprises the 1σ, 2σ, 3σ, and 1π orbitals. The valence space consists of 4σ, 5σ, 2π, and 6σ orbitals which have their origins in the 3*s* and 3*p* valence orbitals of Si and the 1*s* orbital of H. The rest of the higher lying orbitals are excited orbitals. Molecular orbitals are determined by performing self-consistent field (SCF) calculation for the ground $X^2\Pi$ state of neutral SiH. The SCF calculations also produce the orbital energies, and in calculations of H^v and A^v the averaged value of the valence orbital energies is used to guarantee convergence. To understand the influence of basis set size, we have performed calculations at one internuclear distance with the slightly larger aug-cc-pVQZ basis. The fine structure splittings obtained from the aug-cc-pVQZ basis calculations differ only slightly (by less than 3%) from those of aug-cc-pVTZ basis calculations, indicating reasonable basis set convergence. Therefore the current aug-cc-pVTZ basis set is accurate enough for SiH system.

The present calculations follow the common approximation of neglecting the two-electron contributions to the spin-orbit coupling operator (the second term in (9)), which describe the interaction between the spinning motion of an electron and the orbiting motions of other electrons. To compensate for the neglect of the two-electron term, an effective nuclear charge is introduced in the computations of the one-electron spin-orbit coupling integrals as is customary. The effective nuclear charges used are 1.0 au for H and 12.25 au for Si as obtained from the studies of Gordon and coworkers.[18-21]

Sun and Freed's test H^v calculations on SiH at a fixed internuclear distance shows that the introduction of the above effective nuclear charges recovers the most of contributions from the two-electron term.[5]

The effective valence shell wave functions and therefore the energies of valence states are evaluated using the H^v perturbation expansion through second order in correlation (*V*). Previous papers document the good accuracy of these energies for the potential energy curves of the monohydrides.[22-25] The matrix elements of A^v (spin-orbit) are evaluated in the basis of spin-orbitals through first order in the perturbation *V* due to electron correlation. The spin-orbit perturbed valence space CI matrix elements (diagonal and off-diagonal) are the sums of H^v and A^v matrix elements between the valence space eigenfunctions of H^v to include all spin-orbit interactions among the valence states in our calculations.

The spin-orbit coupling energy, of course, depends on the geometry of a molecule, *e.g.*, the internuclear distance between two atoms in a diatom. The A^v calculations are performed at equilibrium internuclear distances (R_e) of all unperturbed (without spin-orbit coupling) bound or quasi-bound valence states of SiH, SiH^+, and SiH^{2+}. The repulsive states and singlet or Σ states that exhibit zero spin-orbit coupling are not of interest in the present calculations. For example, SiH has many bound states which are $X^2\Pi$, $a^4\Sigma^-$, $A^2\Delta$, $B^2\Sigma^-$, $C^2\Sigma^+$, $D^2\Sigma^+$, $E^2\Sigma^+$, $c^4\Sigma^-$, $e^4\Pi$, $f^4\Delta$, *etc*.[26] Omitting Σ states, we have performed calculations for $X^2\Pi$, $A^2\Delta$, $e^4\Pi$, and $f^4\Delta$ states only. For SiH^+, the states of interest are $a^3\Pi$,

Table 1. Fine structure splittings (cm^{-1}) of bound and quasi-bound valence states of SiH, SiH^+, and SiH^{2+} at the equilibrium internuclear distance (R_e) in au

State (Ω)	R_e	This work	Others
SiH			
$X^2\Pi$(1/2, 3/2)	2.87175[a]	144.24	146.68[b], 142.39[c], 142.83[d]
$A^2\Delta$(3/2, 5/2)	2.8719708[e]	8.50	3.58[f]
$b^4\Pi$(1/2, 1/2, 3/2, 5/2)	repulsive[g]	60.86	
$e\Pi^4$(5/2, 3/2, 1/2, 1/2)	2.8501[h]	45.31	
$f^4\Delta$(1/2, 3/2, 5/2, 7/2)	2.9376[h]	9.06	
SiH^+			
$a^3\Pi(0^+/0^-, 1, 2)$	2.906[i]	98.07	95.95[b]
$c^3\Pi(0^+/0^-, 1, 2)$	3.539[i]	101.62	
$1^3\Delta$(1, 2, 3)	3.698[i]	13.86	
$2^3\Delta$(1, 2, 3)	3.144[i]	10.66	
SiH^{2+}			
$A^2\Pi$(1/2, 3/2)	3.50[j]	224.97	
$a^4\Pi$(1/2, 1/2, 3/2, 5/2)	4.06[j]	86.81	

[a]Ref. 30. [b]Theoretical MCSCF value. Effective nuclear charge (au) used = 1.0(H), 3.60(C), 12.25(Si). R_e(au) = 2.1163(CH), 2.1469(CH^+), 2.8724(SiH), 2.8724(SiH^+). Ref. 18. [c]Theoretical MCSCF-ECP value. Effective nuclear charge (au) used = 1.0(H), 3.90(C), 168(Si), 1312(Ge). R_e(au) = 2.1163(CH), 2.1469(CH^+), 2.8726(SiH), 3.0009(GeH). Ref. 21. [d]Experimental value. Ref. 31. [e]Ref. 32. [f]Theoretical MRCI value. Ref. 36. [g]Repulsive state. Splittings computed at R=2.8501au which is the equilibrium distance of the $e^4\Pi$ state for the purpose of comparison. See the text. [h]Ref. 26. [i]Ref. 27. [j]Ref. 29.

$c^3\Pi$, $1^3\Delta$, and $2^3\Delta$.[27,28] SiH^{2+} has two quasi-bound states of $A^2\Pi$ and $a^4\Pi$ for which our calculations are peformed.[29] For quasi-bound states, the equilibrium internuclear distance is the distance where the local minimum of potential energy curve is located.

The calculated fine structure splittings for the valence states of SiH, SiH^+, and SiH^{2+} are presented in Table 1. As mentioned before, singlet (S=1) or Σ (Λ=1) states which have no fine structure splittings are not listed. The traditional definition of the fine structure splitting is the spacing between two adjacent Ω fine structure states. Table 1 presents the intervals between the Ω fine structure levels in the order of increasing energy. For example, the entry (1/2, 3/2) in the first row of the Table 1 means that the Ω=1/2 state lies lower than the Ω=3/2 state. For the $a^3\Pi$ of SiH^+, ($0^+/0^-$, 1, 2) means that the $\Omega=0^+$ and $\Omega=0^-$ states which are degenerate (but are not necessarily degenerate in general) lie lowest and the Ω=1 state lies higher, while the Ω=2 state lies highest. For each state, spin-orbit coupling produces various Ω states but their intervals (equal to the fine structure splittings) always emerge as the same.

In SiH, the $X^2\Pi$ state exhibits a larger fine structure splitting than that of $A^2\Delta$, as expected. The trend is the same for quartet states, *e.g.*, $e^4\Pi$ and $f^4\Delta$. In SiH^+, the splitting for Π states is again much larger than that of Δ states. The $a^4\Pi$ state of SiH^{2+} has four fine structure levels of Ω=1/2, 1/2, 3/2, and 5/2. The two Ω=1/2 states are not degenerate. However, $\Omega=0^+$ and $\Omega=0^-$ are always degenerate, for example, see $a^3\Pi$ of SiH^+. In Table 1 the splitting for the $b^4\Pi$ state is also listed although this is a repulsive state. The fine structure splitting of $b^4\Pi$ is computed at the distance of 2.8501au which is the equilibrium internuclear distance of $e^4\Pi$. Obviously the two splittings are different because they are two different states. It is interesting to note that the ordering of Ω sublevels of the two states is reversed. For atoms, when two states of the same symmetry interact with each other, the ordering of fine structure levels of two states are usually reversed.[33] The energy gap between $b^4\Pi$ and $e^4\Pi$ states is 0.031au so that the two states lie very closely in energy. We see the same phenomenon here in diatomic system. The $a^3\Pi$ and $c^3\Pi$ of SiH^+ have the same ordering of fine structure levels because the two states lie very far from each other (see the R_e in Table 1).

Our calculated splitting of 144.24 cm^{-1} for the ground $X^2\Pi$ state of SiH is in very good agreement with experimental value[31] of 142.83 cm^{-1}. Gordon and coworkers' MCSCF calculations[18,21] produced similar values of 146.68 and 142.39 cm^{-1}. Baeck and Lee's four-component Dirac-Fock calculations[34] also yielded a reasonable value of 148.6 cm^{-1}. (For Dirac-Fock calculations, see Ref. 35). For the $A^2\Delta$ state for which experiment is not available, our splitting is 8.50 cm^{-1} while Marian and coworkers' theoretical splitting[36] is 3.58 cm^{-1}. Marian's CI calculation is a totally different approach from the current A^v so that the direct comparison of two values may be meaningless. For the $a^3\Pi$ state of SiH^+, the MCSCF calculations produce the splitting of 95.95 cm^{-1} while our splitting is 98.07 cm^{-1}. These two values coincide with each other very well. For the highly excited states of SiH and SiH^+, experimental or theoretical data are not available. The $A^2\Pi$ and $a^4\Pi$ states of SiH^{2+} for which we have first determined the fine structure splittings are quasi-bound states. These states are not experimentally found yet because their lifetime should be very short. Our splitting for the $A^2\Pi$ state is 224.97 cm^{-1} which is amazingly large. This must be due to the lone pair electron in 5σ orbital whose spin (s=1/2) produces a magnetic field coupled with its orbiting motion strongly. Overall our A^v calculated values are in good agreement with experiment and other theoretical values although scant experimental data are available.

Conclusions

The effective valence shell spin-orbit Hamiltonian method H^v has been applied to determine the fine structure splittings of all bound and quasi-bound valence states of SiH, SiH^+, and SiH^{2+}. For the low-lying states our calculated fine structure splittings agree very well with experiment or other theories. Our calculations provide fine structure splittings for a wide range of excited and ion states for which there are no prior experimental data or computations. Also the ordering of the fine structure Ω sublevels are predicted for spin-orbit perturbed valence states for the first time. It is interesting to construct a composite picture of potential energy curves. We will report H^v calculations on potential energy curves for all

spin-orbit perturbed valence states of SiH species including repulsive states in the near future.

The present work verifies that the new H^v perturbation approach for calculating spin-orbit couplings properly include off-diagonal spin-orbit matrix elements that are important in predissociation and other non-adiabatic processes. This H^v approach shows how to deal with the complex problem arising from the fact that the perturbation due to electron correlation influences the effective spin-orbit operator. Though only the one-electron spin-orbit operator is used (with a proper effective nuclear charge) to calculate the fine structure splittings, the calculations show very satisfactory agreement with experiment. It suffices to demonstrate that the new effective valence shell spin-orbit Hamiltonian method performs very well.

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