Ab Initio Effective Hamiltonian Calculations on the Valence States of SiH, SiH⁺, PH and PH⁺

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The second order ab initio effective valence shall Hamiltonian (H^v) which is based on quasidegenerate many-body perturbation theory is applied to the SiH, PH, and their positive ions. A single H^v computation for the neutral molecule is used for a whole set of valence states of a molecule and its ion simultaneously. The low-lying valence state potential energy curves of SiH, PH and their positive ions are computed. And various spectroscopic constants of the low-lying bound valence states are determined from the potential energy curves. The H^v results are found to be in good agreement with other theoretical and experimental data.

Introduction

The ab initio effective valence shell Hamiltonian (H^v), based on quasidegenerate many-body perturbation theory (QD-MBPT),[1-3] has been applied to the various atoms,[4-7] diatomic molecules,[8-18] triatomic molecules[19,20] and π-electron system (trans-butadiene).[21-23] Form these applications it is understood that the H^v method is exact in principle and accurate for theoretically calculating electronic structures of molecules. The interesting characteristics of the effective valence shell Hamiltonian (H^v) method is the fact that a single computation for a neutral molecule simultaneously provides accurate energies of all valence states of the molecule and its ions by using the same set of valence orbitals, and thus reduces computational CPU time by a lot.

In the present study we have applied the second order H^v to the diatomic monohydrides *e.g.*, SiH, SiH⁺, PH, and PH⁺ which contain second row atoms. Diatomic hydrides containing second row atoms have never been studied by the H^v method. The potential energy curves for the valence states of these diatoms are computed. Of course, these astrophysically important SiH and PH molecular systems have been studied by various theoretical methods before.[24-27] Nevertheless we take the SiH and PH to investigate the features of ab initio effective valence shell Hamiltonian.

Small radicals and their positive ions have gained increased interests over the past years in both experimental and theoretical studies because of their importance in astrophysical processes and in many chemical reactions.[27] The SiH system is of considerable interest because it exists in stellar atmospheres[24-26] and furthermore this hydride is the smallest fragment of various large silanes which are of increasing importance in modern chemistry. Our H^v calculations exhibit an interesting feature of a double potential well in the $^2\Sigma^+$ state of SiH. The PH radical is interesting because of it $1\sigma^2 2\sigma^2 3\sigma^2 1\pi_x^2 1\pi_y^2 4\sigma^2 5\sigma^2 2\pi^2$ electronic configuration, which leads to three low-lying electronic states of $X^3\Sigma^-$, $a^1\Delta$, and $b^1\Sigma^+$. The singlet states possess long life-time because direct combination with the ground state, just as in the well-known case of O_2, is not an allowed process.

Valence state energies and spectroscopic constants determined in our calculations are all found to agree quite well with experimental[30-35] and theoretical data.[36-43] We first briefly introduce the theory of H^v, and computional procedure is explained, in detail, in the following section. The analyses on H^v calculational results for SiH, SiH⁺, PH, and PH⁺ are provided in Results section. The conclusion is summarized in the final section.

Theory

In Hilbert space all electron configuration can be divided into the primary space with a projector (P) and the complementary space (Q=1-P). The P space is defined as the valence space of all distinct configuration state functions involving a filled core and the remaining electrons distributed among the valence orbitals. The Q space contains all configurations with at least one core hole and/or one occupied excited orbital. The full molecular Schrödinger equation is written as,

$$H\Psi = E\Psi \qquad (1)$$

corresponds to matrix representation as

$$HC = EC, \qquad (2)$$

where C is a vector of coefficients. Schrödinger Eq. (1) can then be expressed in supermatrix form as

$$\begin{pmatrix} H_{PP} & H_{PQ} \\ H_{QP} & H_{QQ} \end{pmatrix} \begin{pmatrix} C_P \\ C_Q \end{pmatrix} = E \begin{pmatrix} C_P \\ C_Q \end{pmatrix}, \qquad (3)$$

where $H_{PP} = \langle \phi_i | H | \phi_{i'} \rangle$ for i, i' P denotes the sub-block of the Hamiltonian matrix within P space, $H_{PQ} = \langle \phi_i | H | \phi_j \rangle$ for $i \in P$, $j \in Q$ that between P and Q, etc. After rearranging (3), we can formally solve this equation to give the partitioned Hamiltonian

$$H^v C_P \equiv [H_{PP} + H_{PQ}(E1_Q - H_{QQ})^{-1} H_{QP}] C_P = E C_P, \qquad (4)$$

where 1_Q is a unit matrix in the Q space. Eq. (4) involves the effective Hamiltonian, H^v, defined only in P space, and has eigenvalues E identical to those of the full Schrödinger Eq. (1). The formulation of Eq. (4) enables H^v to be studied directly. Eq. (4) presents an energy (E) dependent representation of H^v which has a number of computational virtues in being nonperturbative in nature and in taking care of the nonvalence "intruder" states. However, it suffers from not permitting direct calculation of energy- and configura-

tion-independent individual matrix elements of H^v. This difficulty may be overcome by utilizing perturbative expansions and considering energy independent forms of (4).

We now specialize to P being the valence space where all ϕ_i P involve a filled core with the remaining electrons distributed among a set of valence shell orbitals. The choice of what constitutes the core and valence shell is arbitrary as is the choice of core and valence orbitals. Nevertheless, given a specification of these quantities, H^v in (4) still provides the exact energies of the orginal Hamiltonian. H^v of (4) is then the matrix representation of the valence effective shell Hamiltonian. In terms of the restricted P space wavefunctions

$$\Psi^v = \sum_{i \in P} C_i \phi_i, \tag{5}$$

the Eq. (4) is equivalent to

$$H^v \Psi^v = E \Psi^v. \tag{6}$$

The eigenfunctions, Ψ^v of H^v represent the P space projection of the exact eigenfunctions Ψ of (1).

With the aid of QDMBPT, we can expand (4) to obtain energy independent form of H^v. The inverse matrix in Eq. (4) can be expanded with respect to a certain reference energy, E_o, to obtain an (equivalent) energy independent from of H^v. This proceeds by dividing the full Hamiltonian into two parts.

$$H = H_o + V, \tag{7}$$

where H_o is a zeroth-order Hamiltonian (possibly a one-electron operator) and V is the perturbation. When H_o is chosen to be a Fock operator, V represents the so called "correlation energy". The (7) can be projected onto the P. Then the resulting H^v is

$$H^v = PH_oP + PVP + PVQ(E - H_o)^{-1}QVP + \cdots. \tag{8}$$

Then, quasidegenerate many-body perturbation theory gives the second order approximation

$$H^v = PHP + \frac{1}{2} \sum_{\Lambda, \Lambda'} [P(\Lambda)VQ(E - H_o)^{-1}QVP(\Lambda') + h.c.], \tag{9}$$

where h.c. designates the Hermitian conjugate of the preceding term and $P(\Lambda)$ designates the projector onto the valence space basis function $|\Lambda\rangle$

It can be shown that the Eq. (4) has matrix elements between determinantal functions which differ by 0, 1, 2, 3, $\cdots$, n_v valence shell orbitals, where n_v is the number of electrons in the valence shall, *i.e.*, in the P space. This, therefore, implies that the operator form of H^v cannot be represented solely in terms of one- and two-electron interactions, H_i^v and H_{ij}^v (molecular interal operator). In general H^v must contain three-, $\cdots$, n_v-electron operators.

$$H^v = E_c + \sum_{i=1}^{n_v} H_i^v + \frac{1}{2!} \sum_{i \neq j=1}^{n_v} H_{ij}^v + \frac{1}{3!} \sum_{i \neq j \neq k=1}^{n_v} H_{ijk}^v + \cdots, \tag{10}$$

Where E_c is the core energy, H_{ijk}^v is a three-electron operator, etc. Since the 4σ, 5σ, 2π, and 6σ shell is chosen as the valence space for the second row diatomic hydrides, H^v only has matrix elements within 4σ, 5σ, 2π, and 6σ basis for the second row diatomic hydrides. For example, the only nonzero one-electron matrix are $\langle 4\sigma|H_i^v|4\sigma\rangle$, $\langle 5\sigma|H_i^v|5\sigma\rangle$,

$\langle 6\sigma|H_i^v|6\sigma\rangle$, $\langle 4\sigma|H_i^v|5\sigma\rangle$, $\langle 4\sigma|H_i^v|6\sigma\rangle$, $\langle 5\sigma|H_i^v|6\sigma\rangle$ and $\langle 2\pi_x|H_i^v|2\pi_x\rangle = \langle 2\pi_y|H_i^v|2\pi_y\rangle$, since the $\langle 4\sigma|H_i^v|2\pi\rangle$ and $\langle 2\pi_x|H_i^v|2\pi_y\rangle$, etc. vanish by symmetry (through the infinite order in perturbation theory). Similarly the two-electron parts, H_{ij}^v and three electron parts, H_{ijk}^v, only have matrix elements which do not vanish by molecular symmetry. Within the second order approximation of H^v, no four- and higher-electron interaction terms appear.

Note that, once the matrix elements of H_i^v, H_{ij}^v, H_{ijk}^v, $\cdots$, have been evaluated, it is then a straightforward task to diagonalize H^v, using Eq. (6), to obtain the valence shell energies. Although H^v may have been evaluated through a calculation for one particular set of valence orbitals (*e.g.*, those valence orbitals could be chosen from the set of self-consistent field (SCF) orbitals for the ground state of the neutral molecule), the same H^v can be utilized for all charge states of the system (*i.e.*, the ions). It means that we do not need a separate ab initio calculation for each charge state. H^v is, in principle, exact for all these charge states, so if the primitive orbital basis is sufficiently good, H^v should represent them well provided the approximations in treating the Q space in Eq. (4) are not too severe. An investigation of the nature of the representation of these different charge states is one of the motivations of the present research. The detailed second order expressions for each effective operator in (10) are given in Reference 5.

Computations

For Si and P, a basis set of Gaussian-type function is taken from the No. 8 of Veillard's 6s4p functions[44] contracted from 12s9p primitive Gaussians. Additional one s, one p and two d functions are added to the phosphorus[45] and silicon[28] basis, respectively. For hydrogen, Huzinaga's 3s basis functions,[46] which are contracted from the 5s primitive Gaussians, are augmented by one p and one d function. This kind of basis set is called the triple zeta plus polarization basis. The 46 basis functions (7s5p2d/3s1p1d) for SiH and PH are appro- priate for the current H^v calculations. The exponents and contraction coefficients of these basis sets for SiH and PH are given in Tables 1 and 2, respectively.

With the basis set, the SCF calculations are performed for the ground $X^2\Pi$ state of SiH and the ground $X^3\Sigma^-$ state of PH to obtain a set of molecular orbitals. Since the SiH and PH have an open shell structure at the ground state, appropriate vector coupling coefficients are given before the SCF procedure. The Fock operator gives molecular orbitals including virtual orbitals which are not occupied in the ground state SCF configuration. It also generates orbital energies for all the molecular orbitals.

For SiH and PH we adopt the second order H^v formalism. In H^v calculations the valence space consists of configuration state functions arising from 4σ, 5σ, $2\pi_x$, $2\pi_y$, and 6σ orbitals, which contain a full distribution of the five and six valence electrons for SiH and PH, respectively. this choice is appropriate because these molecular orbitals come from valence orbitals of Si and P (3s and 3p) and H (1s). The core orbitals are predetermined as 1σ, 2σ, 3σ, $1\pi_x$, and $1\pi_y$ orbitals and core electronic configuration is fixed as filled, *i.e.*, $1\sigma^2 2\sigma^2 3\sigma^2 1\pi_x^2 1\pi_y^2$ all the way. 7σ and higher-lying orbitals are classified as excited orbitals.

Table 1. Gaussian Basis Set Employed in SiH Calculations[a]

type	Si		H	
	exponents	contraction coefficients	exponents	contraction coefficients
s	69989.300000	0.000310	33.644400	0.023654
s	10380.200000	0.002490	5.057960	0.179767
s	2330.010000	0.013030	1.146800	0.86080
s	657.466000	0.052270	0.321144	1.00000
s	214.004000	0.161510	0.101309	1.00000
s	77.606400	0.347670		
s	30.639500	0.404450		
s	12.815600	0.162430		
s	3.927140	1.00000		
s	1.452210	1.000000		
s	0.257644	1.000000		
s	0.094404	1.000000		
s[b]	0.014000	1.000000		
p	337.495000	0.003540		
p	78.687100	0.027540		
p	24.935100	0.116490		
p	9.215150	0.293300		
p	3.615260	0.432750		
p	1.451990	0.305720		
p	0.503992	1.000000		
p	0.186040	0.564120		
p	0.065432	0.384650		
p[b]	0.014000	1.000000	0.250000	1.000000
d[b]	0.850000	1.000000	0.600000	1.000000
d[b]	0.300000	1.000000		

[a]Ref. 44, [b]Ref. 28.

Table 2. Gaussian Basis Set Employed in PH Calculations

type	P[a]		H[b]	
	exponents	contraction coefficients	exponents	contraction coefficients
s	77718.000000	0.000320	33.644400	0.02365
s	11609.300000	0.002550	5.057960	0.179767
s	2644.290000	0.013140	1.146800	0.860803
s	753.328000	0.051950	0.321144	1.000000
s	248.525000	0.158090	0.101309	1.000000
s	91.069800	0.340990		
s	36.191600	0.404630		
s	15.206300	0.171140		
s	4.713780	1.000000		
s	1.783160	1.000000		
s	0.343249	1.000000		
s	0.125204	1.000000		
s[c]	0.170000	1.000000		
p	385.322000	0.003700	0.735824	1.000000
p	90.626900	0.028580		
p	28.778800	0.121490		
p	10.664390	0.302140		
p	4.243610	0.433690		
p	1.737690	0.290890		
p	0.595843	1.000000		
p	0.228550	0.562390		
p	0.083760	0.319430		
p[c]	0.0154000	1.000000		
d[c]	0.850000	1.000000	0.650000	1.0000000
d[c]	0.300000	1.000000		

[a]Ref. 44, [b]Ref. 46, [c]Ref. 45.

The zeroth order Hamiltonian chosen in H^v formalism is a diagonal one-electron operator. Since H^v describes all the valence states on an equal footing, only one SCF calculation is necessary enough for producing all other valence states. The same set of molecular orbitals are used for both of SiH and SiH^+ and for both of PH and PH^+. In the second order H^v calculations, orbital energies for SiH and PH molecular orbitals are taken from the diagonal elements of Fock operator of the ground $X^2\Pi$ state of neutral SiH and the groud $X^3\Sigma^-$ state of neutral PH molecule, respectively. To guarantee the fast convergence of the second order H^v, orbital energies for the valence orbitals (4σ, 5σ, $2\pi_x$, $2\pi_y$, and 6σ) are arithmetically averaged.

The second order H^v matrix element are composed of the core energy (E_c), one-electron (H^v_i), two-electron (H^v_{ij}), and three-electron matrix elements (H^v_{ijk}). The core energy is the energy of $1\sigma^2 2\sigma^2 3\sigma^2 1\pi_x^2 1\pi_y^2$ configuration including all the core-core, core-valence, and core-excited correlations. The three-electron H^v matrix elements should exist because the H^v is the effective Hamiltonian, ,which means that the whole H operator is projected onto the small valence space, P. In the second order H^v expression, the four- or higher-electron terms do not appear. With these H^v matrix elements, we can set up the small valence configuration interaction (CI) matrix. After diagonalizing the valence CI matrix (Eq. (4)),

we can obtain the valence state energies. All the valence state enegies are calculated with a same accuracy. Next, the nuclear repulsion energy is added to them in order to obtain the total energies of valence states. For ions, i.e., SiH^+ and PH^+, similar CI matrix is set up and diagonalized. The only difference between a neutral molecule and its ion is the number of valence electrons. Same H^v matrix elements are used for both of a neutral molecule and its ion.

The whole procedure has been repeated by changing internuclear distance between Si and H and between P and H. The internuclear distances (R) where H^v calculations were performed are 2.25, 2.5, 2.7, 2.8, 2.8726, 2.9, 3.0, 3.5, 4.0, 4.5, and 5.0 au for SiH and 2.0, 2.25, 2.5, 2.6, 2.7, 2.85, 3.0, 3.5, 4.0, 4.5, and 5.0 au for PH, respectively. H^v calculation for atomic Si, P and H are separately performed to determine separate atom limits correctly. And potential energy curves are interpolated between R=5.0 au and separate atom limits.

Spectroscopic constants for several low-lying states of SiH, SiH^+, PH and PH^+ were determined by fitting the calculated potential energy curves to an eighth degree polynomial. Form this, Dunham coefficients are computed to obtain R_e, ω_e, $\omega_e\chi_e$, B_e, α_e and D_e values.

In summary, the step-by-step computation procedure is as follws: i) Choose the basis set. ii) Perform the SCF calculation for the ground state of SiH or PH to obtain molecular

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Table 3. Second Order H^v Total Energies (au) of SiH as a Function of Internuclear Distance, R (au)

R	$X^2\Pi$	$a^4\Sigma^-$	$A^2\Delta$	$B^2\Sigma^+$	$^2\Sigma^+$
2.25	−289.613560	−289.564344	−289.509257	−289.465399	−289.443089
2.5	−289.654554	−289.602624	−289.549263	−289.505291	−289.482945
2.7	−289.669042	−289.615908	−289.564568	−289.520419	−289.496539
2.8	−289.672761	−289.618969	−289.568764	−289.524557	−289.499074
2.8726	−289.674224	−289.619727	−289.570347	−289.526144	−289.499795
2.9	−289.672635	−289.617854	−289.568803	−289.524578	−289.500872
3.0	−289.671555	−289.614992	−289.566941	−289.524300	−289.500112
3.5	−289.665369	−289.601957	−289.557934	−289.524406	−289.500176
4.0	−289.645975	−289.591071	−289.552037	−289.537312	−289.494219
4.5	−289.615023	−289.574655	−289.539112	−289.532207	−289.478212
5.0	−289.594245	−289.568227	−289.534668	−289.529781	−289.469806
∞	−289.561971	−289.561971	−289.527988	−289.527988	−289.469530

R	$^2\Sigma^-$	$^4\pi$	$^2\pi$	$^4\Sigma^-$	$^b\Sigma^-$
2.25	−289.491914	−289.369741	−289.361630	−289.303562	−289.073103
2.5	−289.529682	−289.409903	−289.402511	−289.365792	−289.128277
2.7	−289.549943	−289.425926	−289.417897	−289.397609	−289.157777
2.8	−289.554011	−289.431390	−289.421731	−289.409649	−289.171123
2.8726	−289.557526	−289.434023	−289.422686	−289.416901	−289.181088
2.9	−289.558324	−289.434718	−289.420691	−289.417330	−289.183337
3.0	−289.560988	−289.437164	−289.417116	−289.423462	−289.197816
3.5	−289.561142	−289.483883	−289.450357	−289.444585	−289.290580
4.0	−289.561437	−289.522916	−289.491466	−289.445702	−289.340647
4.5	−289.561622	−289.536058	−289.506683	−289.426872	−289.357932
5.0	−289.561761	−289.546061	−289.517533	−289.411043	−289.368759
∞	−289.561971	−289.561971	−289.527988	−289.390126	−289.390126

orbitals. iii) Evaluate molecular integrals and orbital energies. iv) Compute the second order H^v matrix elements. v) Set up a valence CI matrix with the H^v matrix elements. vi) Similar valence CI matrix can be set up for the SiH^+ or PH^+ ion, too. vii) Diagonalize the valence CI matrix. viii) Add the nuclear repulsion energy to the eigenvalues of the CI matrix to have the valence state energies. ix) A whole calculation is repeated at various internuclear distances to generate the potential energy curves. x) From the potential energy curves, dissociation energies and spectroscopic constants are determined by calculating Dunham coefficients.

Results

SiH and SiH⁺. For the ground $X^2\Pi$ state of SiH at equilibrium internuclear distance (R=2.8726 au), our SCF energy is −289.4139 au. It is higher than that of Meyer and Rosmus's[37] (SCF energy= −289.430283 au at R=2.8 au), of Larsson's[39] (SCF energy= −289.432082 au at R=2.87 au) and of Lewerenz et al.'s[28] (SCF energy= −289.4149 au at R=2.855 au) calculated with a large basis set including f basis function. But our value is lower than Mavridis and Harrison's SCF energy[40] (−289.41082 au) and Wirsam's value[41] (−289.3150 au). The SCF energy for the ^3P state of Si is −288.8334 au and it is higher than that of Lewerenz et al.'s[28] (−288.8341 au). The total energies for the several val-

ence states of SiH and SiH^+ at various internuclear distances and separate atom limits are listed in Tables 3 and 4, respectively. At R_e=2.878 au the total energy for the $X^2\Pi$ state of SiH is −289.6730 au. Mayer and Rosmus' energy[37] is −289.53387 au (PNO-CI) and −289.54077 au (CEPA), Lewerenz et al.'s energy[28] is −289.5125 au (MRD-CI), and Larsson's value[39] is −289.541256 au (CAS-CI). Even though they used a large basis set including f function, their total energy is higher than ours. Correlation energy is the difference between the SCF energy and the total energy. The second order H^v correlation energy for the SiH ground state is 0.25908 au at equilibrium distance. In Lewerenz et al.'s[28] it is 0.1046 au (full CI) and 0.0990 au (MRD-CI). Meyer and Rosmus's correlation energy[37] is 0.1028 au (PNO-CI) and 0.1102 au (CEPA).

The total energy for the ground $X^1\Sigma^+$ at R=2.845 au is −289.3853 au. Mauricio et al.'s value,[47] which was calculated using a large basis set (12s7p4d1f/8s4p2d) at R=2.80 au, is −289.357073 au (MBPT) and −289.351508 au (CASSCF). Hirst's value[48] is −289.247867 au at R=2.8346 au with a basis set of 6s5p2d/3s2p. Rosmus and Meyer's value[49] is −289.247698 au (PNO-CI) and −289.252736 au (CEPA). Gordon's value[50] is −288.78593 au at R=2.939 au. The difference between the energy for the $X^2\Pi$ state of SiH and that for the $X^1\Sigma^+$ state of SiH^+ at equilibrium distance is adiabatic ionization potential. Our ionization potential (I.P.=7.90

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Table 4. Second Order H^v Total Energies (au) of SiH^+ as a Function of Internuclear Distance, R (au)

R	$X^1\Sigma^+$	$a^3\Pi$	$A^1\Pi$	$b^3\Sigma^-$	$c^3\pi$	$^3\Sigma^+$	$^1\Delta$
2.25	−289.328929	−289.252453	−289.214637	−289.106858	−288.979977	−288.938137	−289.061953
2.5	−289.369324	−289.292749	−289.260173	−289.145983	−289.041706	−288.983879	−289.099278
2.7	−289.382938	−289.307537	−289.279865	−289.162004	−289.072309	−289.010150	−289.111549
2.8	−289.386150	−289.311294	−289.286049	−289.162615	−289.083798	−289.024870	−289.113766
2.8726	−289.387253	−289.312543	−289.288880	−289.163688	−289.090864	−289.037549	−289.113822
2.9	−289.385551	−289.310879	−289.287717	−289.161125	−289.091385	−289.041052	−289.111779
3.0	−289.384147	−289.308768	−289.287024	−289.157724	−289.098348	−289.062323	−289.108191
3.5	−289.374076	−289.298928	−289.277555	−289.145991	−289.124499	−289.169673	−289.100591
4.0	−289.347802	−289.289948	−289.275306	−289.133505	−289.120250	−289.214116	−289.088362
4.5	−289.311552	−289.273059	−289.264599	−289.109428	−289.099190	−289.228161	−289.063588
5.0	−289.286966	−289.264093	−289.259625	−289.092298	−289.084665	−289.237836	−289.047258
∞	−289.259388	−289.259388	−289.259388	−289.061971	−289.061971	−289.259388	−289.027988

R	$^1\Sigma^+$	$^1\Pi$	$^5\Sigma^-$	$^5\Pi$	$^3\Pi$	$^3\Sigma^-$
2.25	−289.009916	−288.895172	−288.953427	−288.609967	−288.771109	−288.828678
2.5	−289.047532	−288.952663	−289.009355	−288.670015	−288.822182	−288.886203
2.7	−289.060023	−288.979594	−289.035881	−288.709569	−288.846074	−288.909691
2.8	−289.062458	−288.989320	−289.044969	−288.732809	−288.857961	−288.925180
2.8726	−289.106250	−288.995213	−289.049881	−288.753224	−288.867558	−288.931192
2.9	−289.060828	−288.995452	−289.049907	−288.760281	−288.869706	−288.931447
3.0	−289.057885	−289.001210	−289.052441	−289.795975	−288.884708	−288.935733
3.5	−289.054914	−289.034044	−289.070429	−288.954734	−288.966532	−288.958147
4.0	−289.048459	−289.041153	−289.075824	−289.005410	−288.999095	−288.975295
4.5	−289.036753	−289.032414	−289.064279	−289.020738	−289.006935	−288.986090
5.0	−289.033330	−289.030075	−289.062083	−289.029926	−289.018237	−289.003149
∞	−289.027988	−289.027988	−289.060142	−289.060142	−289.060142	−289.060142
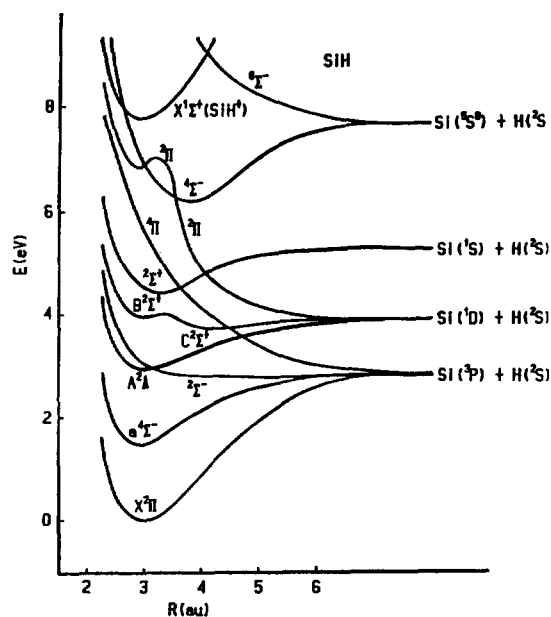
Figure 1. Adiabatic potential energy curves for SiH.

eV) agrees quite well with the experimental value (8.01 ± 0.08 eV). Ramakrishna and Lakshman's ionization potential[36] is 7.91 eV.

This comparison indicates that i) the second order H^v me-
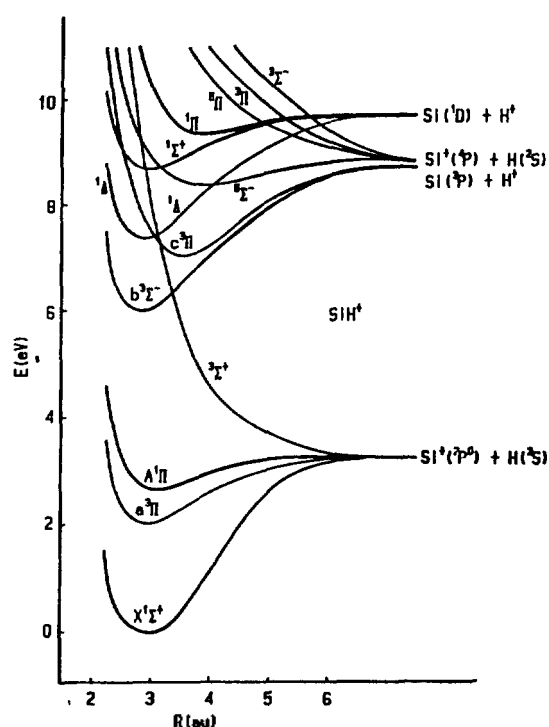
Figure 2. Adiabatic potential energy curves for SiH^+.

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thod is accurate enough to determine that valence state energies and ii) the basis set we chose is practically large and adequate. To test the role of three-electron terms we calculated the above quantities ignoring the three-electron terms and the results were very erroneous. This test shows the importance of the three-electron which should exist in effective Hamitonian theory.

The potential energy curves of SiH and SiH⁺ are plotted in Figure 1 and 2, respectively. In Figures 1 and 2, all the molecular valence states of SiH and SiH⁺ dissociating into the several lowest separate atom limits are presented. In Figure 1 the lowest separate atom limit of $Si(^3P)+H(^2S)$, correlates with the $X^2\Pi$ and $a^4\Sigma^-$ states which are well bound, the $^4\Pi$ state which is strongly repulsive, and the repulsive $^2\Sigma^-$ state.

The second separated atom limit of $Si(^1D)+H(^2S)$ correlates with the $A^2\Delta$, $B^2\Sigma^+$, $C^2\Sigma^+$ and $^4\Pi$ states. The $^2\Sigma^+$ state emerging from the separate atom limit of $Si(^1D)+H(^2S)$ crosses with the $^2\Sigma^+$ state from the $Si(^1S)+H(^2S)$ limit around R=3.5 au. This avoided crossing generates two minima (i.e. $B^2\Sigma^+$ and $C^2\Sigma^+$) in the lower $^2\Sigma^+$ state potential curve. The vertical excitation energy of the first minimum ($B^2\Sigma^+$) and the second shallow minimum ($C^2\Sigma^+$) are 4.02 eV around R= 3.0 au and 3.73 eV around R=4.0 au, respectively. In other theoretical calculations[28,53] the excitation energies are in the range of 3.77-3.95 eV. Experimental T_o values for the $C^2\Sigma^+$ and $B^2\Sigma^+$ states are almost equal (C state lower by 10⁻¹).[55] In our calculations the first potential well, is located around R=3.0 au and the second potential well is located around R=4.0 au. Even though the T_e for the first well is slightly

greater than that for the second well our R_e and ω_e values are similar to the earlier ab initio values.[28,39] Therefore the first potential well is the $B^2\Sigma^+$ state, and the second well is the $C^2\Sigma^+$ state.

The second $^2\Pi$ state potential curve does exhibit a local maximum with a shallow quasi-bound well near the equilibrium distance of the $X^2\Pi$ ground state. The bound $^4\Sigma^-$ and the repulsive $^6\Sigma^-$ states have the separate atom limit of $Si(^5S)+H(^2S)$. The $^4\Sigma^-$ state is bound with a minimum around R=3.78 au, but it has not been characterized experimentally yet.

Among the several valence states of SiH⁺ shown in Figure 2, $X^1\Sigma^+$, $a^3\Pi$, $A^1\Pi$ and $^3\Sigma^+$ states have a seperate atom limit of $Si^+(^2P^o)+H(^2S)$. The lowest three states are bound and they were observed in experiments before.[29,61] The $^3\Sigma^+$ state is found to be purly repulsive. The next lowest dissociation limit. i.e., $Si(^3P)+H^+$, lies very higher than the $Si^+(^2P^o)+H(^2S)$ limit. There are found to be many bound states emanating from this limit. The $^1\Delta$, $^5\Sigma^-$, $^1\Sigma^+$, and $^1\Pi$ states are found to be bound, and these states have not yet been characterized experimentally. As shown in Figure 2, the H⁹ calculation reproduces all the valence state potential curves including the high-lying ones. One should note that the valence states shown in Figures 1 and 2 are determined from a single computation of H⁹ matrix elements. This is a remarkable advantage of the effective valence shell Hamiltonian method over other theoretical methods.

The spectroscopic constants for the bound SiH and SiH⁺ valence states are presented in Tables 5 and 6, respectively. Generally these calculated constants using the second order

Table 5. Spectroscopic Constants for the Lowest Few States of SiH

State		R_e (au)	ω_e (cm⁻¹)	$\omega_e\chi_e$ (cm⁻¹)	B_e (cm⁻¹)	α_e (cm⁻¹)	D_e (eV)	T_e (eV)
$X^2\Pi$	H⁹	2.878	1995.5	37.10	7.72	0.884	3.021	-------
	SCF⁹	2.861	2144.0	30.9	7.56	0.189	2.23	
	PNO-CI⁶	2.878	2061.3	34.1	7.47	0.208	2.99	
	CEPA⁶	2.884	2034.7	36.0	7.44	0.216	3.09	
	MRD-CI⁶	2.918	2015	39.0	7.269	0.208	2.94	
	RKRV⁹	2.873	2041.8	35.51	7.4996	0.219	2.98	
	CASSCF⁹	2.899	1992.6	37.6	7.362	0.228		
	CAS-CI⁶	2.872	2057.8	37.8	7.505	0.218		
	MCSCF⁹		1988.1	39.7	7.257	0.2217		
	POL-CI⁹		1874.8	21.5	7.057	0.2103		
	CI⁶	2.950	2200.0					
	CISD⁶	2.8757	2062					
	SDCI⁶	2.872	2044					
	CPF⁶	2.878	2022					
	exptl⁶	2.873	2041.80	35.51	7.4996	0.219		
	exptl⁶	2.873	2042.0	35.481		0.2156		
	exptl⁶	2.87174	2042.522	26.055	7.395	0.218		
	exptl⁹		2042					
$a^4\Sigma^-$	H⁹	2.818	2562.1	21.68	8.06	0.432	1.544	1.48
	MRD-CI⁶	2.855	2030	65.0	7.595	0.313		1.52
	SCF+1+2⁹	2.868	2019.6	65.9	7.521	0.2885		
	ALIS⁹	2.837	2086.5	76.4	7.689	0.3051		
	POL-CI⁹	2.909	1877.9	62.3	7.313	0.3061		
	ALIS+1+2⁹	2.877	1982.5	60.6	7.476	0.2858		
	CI⁶	2.877	2255					1.04

State	Method	R_e	ω_e	$\omega_e\chi_e$	B_e	α_e	D_e	T_e
A²Δ	H[v]	2.871	2311.8	25.4	7.76	0.535	1.12	2.83
	MRD-CI[c]	2.9215	1797	91.0	7.253	0.420		3.06
	RKRV[d]	2.879	1858.9	99.175	7.4664	0.3445		3.024
	CAS-CI[e]	2.8667	1884.4	68.4	7.473	0.242		
	CI[g]	2.936	1955					3.096
	exptl[m]	2.878	1858.13	98.73				3.00
	exptl[l]	2.879	1858.9	99.175	7.4664	0.3445		3.01
	exptl[p]							3.013
B²Σ⁺	H[v]	2.906	1820.5	76.87	7.50	0.367		4.02
	MRD-CI[c]	2.9347	1550		7.19			3.94
	CI[g]	2.996	1710					3.958
	CI[k]							3.767
	exptl[p]							3.947 (T_o)
C²Σ⁺	H[v]	3.958						3.726
	CI[n]							3.7625
	exptl[p]							3.948 (T_o)
²Σ⁻	H[v]	2.913						3.142
	CI[g]							3.328
	CI[n]							3.179
	exptl[p]							3.066
²Σ⁺	H[v]	2.919	962.1	404.74	7.09	0.652	0.832	4.70
⁴Σ⁻	H[v]	3.778	1792.2	73.61	4.49	0.106	1.589	6.11
	MRD-CI[c]	3.723	1245	22.0	4.47	0.094		6.45

[a]Ref. 36, [b]Ref. 37, [c]Ref. 28, [d]Ref. 38, [e]Ref. 39, [f]Ref. 40, [g]Ref. 41, [h]Ref. 42, [i]Ref. 43, [j]Ref. 30, [k]Ref. 31, [l]Ref. 32, [m]Ref. 33, [n]Ref. 60, [o]Ref. 34, [p]Ref. 35.

Table 6. Spectroscopic Constants for the Lowest Few States of SiH⁺

State		R_e (au)	ω_e (cm⁻¹)	$\omega_e\chi_e$ (cm⁻¹)	B_e (cm⁻¹)	α_e (cm⁻¹)	D_e (eV)	T_e (eV)
X¹Σ⁺	H[v]	2.845	2111.4	30.99	7.91	0.758	3.461	-------
	CASSCF[a]	2.844	2161.23	34.14	7.65	0.20		
	MBPT(4)[b]	2.842	2176.42	37.31	7.67	0.21		
	MR-CI[b]		2155.35	38.82	7.6786	0.2082	3.229	
	RKRV[c]	2.833	2157.10	34.21	7.6603	0.2096		
	PNO-CI[d]	2.848	2175.4	36.7	7.62	0.192		
	CEPA[d]	2.853	2153.5	38.9	7.60	0.203		
	exptl[e]	2.842	2157.15	34.23	7.6576	0.2015	3.22	
	exptl[f]	2.833	2157.10	34.21	7.6603	0.2096		
a³Π	H[v]	2.850	2388.4	25.74	7.88	0.532	1.412	2.014
	MR-CI[b]		1729.79	103.68	7.3553	0.5179	0.985	
	NRD-CI[g]							2.23
A¹Π	H[v]	3.520	509.5	61.28	5.06	1.55	0.780	3.124
	CASSCF[v]	4.03	228.25		3.662	0.275		
	CCI[g]	3.626	355.97		4.341	0.710		
	CEPA[d]	3.596	385.97		4.458	0.780		
	CPF[v]	3.568	438.33		4.637	0.845		
	RKRV[c]	3.547	468.60	39.22	4.9125	0.7667		3.207
	MRD-CI[e]							3.40
	exptl[e]		448.39	30.41	5.003	1.020	0.262	3.208
	exptl[f]	3.536	468.60	39.22	4.9125	0.7667	0.25	

b³Σ⁻	Hʸ	2.782	3019.4	307.46	8.27	0.444	2.758	6.023
	MRD-CIᶠ							6.13
c³Π	Hʸ	3.696	2185.3	91.85	4.69	0.071	1.784	7.013
	MRD-CIᵏ							7.62
¹Δ	Hʸ	2.776	2762.3	343.22	8.30	0.551	2.327	7.396
⁵Σ⁻	Hʸ	3.848	1885.8	133.53	4.32	0.024	0.466	8.382
¹Σ⁺	Hʸ	2.786	2586.3	458.01	8.23	0.736	0.928	8.795
¹Π	Hʸ	3.825	2233.3	167.99	4.37	0.053	0.424	0.298

ªRef. 47, ᵇRef. 48, ᶜRef. 38, ᵈRef. 49, ᵉRef. 29, ᶠRef. 61, ᵍRef. 53, ʰRef. 62.

Table 7. Second Order Hʸ Total Energies (au) of PH as a Function of Internuclear Distance, R (au)

R	X³Σ⁻	a¹Δ	b¹Σ⁺	A³Π	c¹Π	⁵Σ⁻
2.0	−341.411602	−341.363467	−341.333835	−341.261501	−341.218746	−341.099479
2.25	−341.479158	−341.431037	−341.400956	−341.327740	−341.282711	−341.169477
2.5	−341.504573	−341.456505	−341.425959	−341.353560	−341.314924	−341.200247
2.6	−341.507790	−341.459747	−341.429002	−341.357469	−341.321589	−341.206619
2.7	−341.508312	−341.460292	−341.429344	−341.358999	−341.325940	−341.210898
2.85	−341.505354	−341.457374	−341.426113	−341.358162	−341.329366	−341.214599
3.0	−341.499300	−341.451363	−341.419783	−341.354946	−341.330343	−341.216149
3.5	−341.470444	−341.422568	−341.389930	−341.344721	−341.329781	−341.226132
4.0	−341.450018	−341.401335	−341.367770	−341.339262	−341.329219	−341.301717
4.5	−341.429378	−341.378156	−341.343886	−341.338548	−341.328657	−341.364913
5.0	−341.412598	−341.357407	−341.322622	−341.338077	−341.328094	−341.382780
∞	−341.394477	−341.327532	−341.295007	−341.327532	−341.327532	−341.394477

R	³Σ⁻	³Δ	¹Σ⁻	³Π	¹Π	³Σ⁺
2.0	−341.093522	−341.015567	−341.004205	−341.164985	−341.161249	−340.974645
2.25	−341.163566	−341.088341	−341.083547	−341.233588	−341.229910	−341.048033
2.5	−341.193809	−341.122243	−341.123842	−341.260976	−341.257097	−341.082695
2.6	−341.199729	−341.129915	−341.133904	−341.265464	−341.261407	−341.090682
2.7	−341.203358	−341.135485	−341.141704	−341.267571	−341.263267	−341.096570
2.85	−341.205612	−341.141070	−341.150261	−341.267474	−341.262667	−341.105344
3.0	−341.204995	−341.144420	−341.156129	−341.264525	−341.259088	−341.106509
3.5	−341.199431	−341.159098	−341.174871	−341.251081	−341.242490	−341.122985
4.0	−341.258457	−341.233397	−341.239068	−341.278754	−341.265164	−341.198131
4.5	−341.310704	−341.296230	−341.295428	−341.290055	−341.285770	−341.260620
5.0	−341.320047	−341.314973	−341.314550	−341.294180	−341.292122	−341.279223
∞	−341.327532	−341.327532	−341.327532	−341.295007	−341.295007	−341.295007

Hʸ are found to be in quite good agreement with experimental[30-33,43] and theroretical[28,36-40] values.

PH and PH⁺. The SCF energy for the X³Σ⁻ state of PH at R=2.70 au is −341.27003 au. It is higher than earlier SCF calculational result carried out using Slater type basis functions[51]. Our value is also higher than the value reported by Meyer et al.[37] and that by Bruna et al.[45] The total energies for the several valence states at various internuclear distances and separate atom limits are listed in Table 7 for

PH and in Table 8 for PH⁺. At R=2.6717 au our to total energy for the X³Σ⁻ state of PH using second order Hʸ is −341.50840 au. This value is lower than Bruna et al.'s values [45] (−341.3943 au at the MRD-CI and −341.3984 au at the full CI), Meyer and Rosmus's values[37] (−341.41504 au at the PNO-CI and −341.424044 au at the CEPA), and Senekowitsch et al.'s values[52] (−341.4260 au at the MCSCF-CI) calculated with the large basis set including the f basis function.

Table 8. Second Order H^v Total Energies (au) of PH^+ as a Function of Internuclear Distance, R (au)

R	$X^2\Pi$	$^4\Sigma^-$	$^2\Sigma^-$	$A^2\Delta$	$^2\Sigma^+$	$^2\Pi$
2.0	−341.051934	−340.987602	−340.894833	−340.904350	−340.863360	−340.703228
2.25	−341.120648	−341.056632	−340.973092	−340.976027	−340.935672	−340.777615
2.5	−341.146670	−341.084951	−341.011531	−341.007578	−340.968024	−340.811916
2.6	−341.150026	−341.089778	−341.020539	−341.013833	−340.974612	−340.819074
2.7	−341.150623	−341.092151	−341.027084	−341.017685	−340.978795	−340.823681
2.85	−341.147665	−341.092400	−341.033440	−341.020195	−341.981782	−340.827051
3.0	−341.141493	−341.090011	−341.036832	−341.020051	−340.984075	−340.827480
3.5	−341.113889	−341.074874	−341.037693	−341.014405	−340.984675	−340.820180
4.0	−341.087526	−341.060585	−341.035950	−341.004513	−340.984880	−340.862947
4.5	−341.063118	−341.044160	−341.034510	−340.997009	−340.985085	−340.949249
5.0	−341.046076	−341.039195	−341.033683	−340.992352	−340.986184	−340.966771
∞	−341.032400	−341.032400	−341.032400	−340.988237	−340.988237	−340.988237

R	$^4\Pi$	$^2\Pi$	$^4\Sigma^-$	$^2\Sigma^-$	$^2\Sigma^+$	$^2\Delta$
2.0	−340.527331	−340.523325	−340.644156	−340.467362	−340.633324	−340.544022
2.25	−340.607185	−340.603445	−340.745121	−340.559344	−340.706989	−340.642665
2.5	−340.649462	−340.645351	−340.800578	−340.604120	−340.740100	−340.694942
2.6	−340.661374	−340.656612	−340.814642	−340.613719	−340.747561	−340.707568
2.7	−340.671831	−340.665927	−340.825261	−340.619876	−340.753069	−340.716688
2.85	−340.685430	−340.677129	−340.836006	−340.624106	−340.758790	−340.725133
3.0	−340.697108	−340.685549	−340.841958	−340.624000	−340.762246	−340.728804
3.5	−340.747881	−340.721246	−340.843546	−340.616229	−340.780025	−340.723785
4.0	−340.899887	−340.805467	−340.857328	−340.717138	−340.881261	−340.738463
4.5	−340.990106	−340.818001	−340.875655	−340.789288	−340.926017	−340.789493
5.0	−341.007769	−340.825686	−340.884730	−340.811959	−340.915934	−340.816924
∞	−341.032400	−340.827532	−340.894477	−340.827532	−340.916493	−340.827532

In H^v calculations total energy for the ground state ($X^3\Sigma^-$) is found to lie below the present SCF energy by 0.23837 au. This correlation energy is comparable to that obtained in earlier ab initio works, i.e., Meyer's values[37] (0.1275 au at PNO-CI and 0.1365 au at CEPA) and Bruna's values[45] (0.1239 au at MRD-CI and 0.1280 au at full CI). Because the three-electron terms (H^v_{ijk}) in the second order H^v calculations largely contribute to the correlation effects, our correlation energy may be larger than others.

In Table 8 the total energy for the $X^2\Pi$ state of PH^+ at R = 2.6746 au is −341.1507 au. The previous ab initio calculations including f basis functions were performed by Bruna et al.[45] ($E_t = -341.0249$ au at MRD-CI and $E_t = -341.0288$ au at full CI) and Rosmus et al.[49] ($E_t = -341.04729$ au at PNO-CI and −341.05488 au at CEPA). The difference between the energy for the $X^3\Sigma^-$ state of PH and that for the $X^2\Pi$ state of PH^+ at the equilibrium distance is the ionization potential of PH. Our ionization potential is 9.73 eV. This value is similar to the Bruna's[45] (10.05 eV at PNO-CI) and Meyer's value[37] (10.04 eV at CEPA).

The potential energy curves for PH and PH^+ are presented in Figures 3 and 4, respectively. In Figure 3, the $X^3\Sigma^-$ state correlates directly with the first dissociation limit of $P(^4S^0) + H(^2S)$ and its dominant electronic configuration is $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2_x 1\pi^2_y 4\sigma^2 5\sigma^2 2\pi^1_x 2\pi^1_y$. The lowest $X^3\Sigma^-$, $a^1\Delta$ and b^1 Σ^+ states of PH run quite parallel to each other between
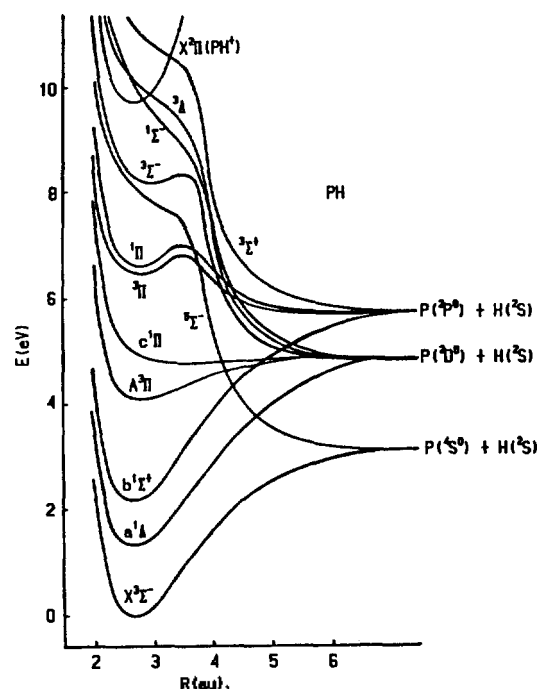

Figure 3. Adiabatic potential energy curves for PH.

Figure 4. Adiabatic potential energy curves for PH⁺.

2.5 and 4.0 au internuclear distance, a situation which is easily understood on the basis of the common electronic con-

figuration. Both of the $a^1\Delta$ and $b^1\Sigma^+$ state potential energy curves remain approximately parallel (with a slight distortion) towards dissociation, in accordance with the fact that the energy separation of 0.91 eV between $^2D^o$ and $^2P^o$ states of isolated P atom is comparable with the $a^1\Delta - b^1\Sigma^+$ splitting at separate atom limits (our value is 0.885 eV). And the shape of our curves and the energy gap between $a^1\Delta$ and $b^1\Sigma^+$ state (0.84 eV) at the equilibrium internuclear distance are similar to those of Bruna's curves[45] (0.86 eV).

The $A^3\Pi$ state crosses the repulsive $^5\Sigma^-$ valence state at an internuclear distance of $R \cong 4.0$ au. The crossing point is located approximately 0.53 eV above the minimum of the $^3\Pi$ state. The potential curve of $c^1\Pi$ state has a shallow minimum, while in the previous calculations[45] this curve is rather flat. It indicates this state has a quasidissociative character. The $^1\Pi$, $^3\Pi$, $^1\Sigma^-$, $^3\Sigma^-$, $^3\Delta$, $^3\Sigma^+$, and $^5\Sigma^-$ states are characterized around $R = 3.7$ au by an avoided crossing with other repulsive states. In the present H^v calculations we did not include Rydberg states.

In PH⁺ curves, $X^2\Pi$ state $(4\sigma^2 5\sigma^2 2\pi^1)$ correlates with the lowest dissociation atom limit of $P^+(^3P) + H(^2S)$. The 5σ and 2π molecular orbitals come from the 3p atomic orbital of an isolated P⁺ ion. The $^4\Sigma^-$ state is found to be well bound which is not characterized experimentally. The $^2\Sigma^-$ and $^2\Sigma^+$ states have quasidissociative character and this fact explains the absence of absorption lines in experiments. The $A^2\Delta$ state is found to be bound, which correlates with the second

Table 9. Spectroscopic Constants for the Lowest Few States of PH

State		R_e (au)	ω_e (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	D_e (eV)	T_e (eV)
$X^2\Sigma$	H^v	2.6717	2448.7	44.67	8.58	0.238	3.10	-----
	SCF^a	2.668	2515	36.37	8.664	0.2145		
	POL-CI^b	2.6853	2408.6	41.7	8.55	0.240	2.93	
	CFPA^b	2.6947	2365.9	44.8	8.49	0.251	3.04	
	MRD-CI^c	2.6883	2380	43.9	8.533	0.254	3.03	
	MCSCF-CI^d	2.6891	2379	42	8.524	0.253	3.05	
	exptl^e	2.6874	2366.8	45.3	8.5327	0.2522	3.17	
	exptl^f	2.6947	2365.9	44.5	8.49	0.251		
$a^1\Delta$	H^v	2.673	2444.5	45.1$^-$	8.570	0.239	3.62	1.30
	MRD-CI^c	2.6793	2415	48.0	8.591	0.269		1.1
	exptl^f	2.703 (R_o)			8.440			
	exptl^h							0.95 (T_o)
$b^1\Sigma^+$	H^v	2.6637	2476.2	44.4	8.628	0.236	3.66	2.14
	MRD-CI^c	2.6723	2438	48.0	8.637	0.260		1.96
	exptl^h							1.78 (T_o)
$A^3\Pi$	H^v	2.7341	2052.7	88.7	8.176	0.367	0.86	4.06
	MRD-CI^c	2.7250	2071	80	8.259	0.473		3.86
	MCSCF-CI^d	2.7325	2029	87	8.262	0.450	0.86	3.69
	exptl^e	2.7322	2030.6	98.5	8.259	0.473	0.89	3.66
$c^1\Pi$	H^v	3.0					0.076	4.85
	MRD-CI^c							5.06
	J-L^j							4.72

^{a}Ref. 36, ^{b}Ref. 37, ^{c}Ref. 45, ^{d}Ref. 52, ^{e}Ref. 56, 57, ^{f}Ref. 34, 63, ^{g}Ref. 54, ^{h}Ref. 64.

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Table 10. Spectroscopic Constants for the Lowest Few States of PH$^+$

State		R_e (au)	ω_e (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	D_e (eV)	T_e (eV)
X$^2\Pi$	H^v	2.6746	2472.1	40.2	8.56	0.215	3.22	-----
	PNO-CI^a	2.6966	2412.8	43.2	8.47	0.224	3.32	
	CFPA^a	2.7042	2375.8	44.9	8.42	0.235		
	MRD-CI^b	2.6921	2354	47.2	8.509	0.271		
	exptl^c	2.7121 (R$_o$)	2299.6		8.3851			
$^4\Sigma^-$	H^v	2.7835	1963.0	72.5	7.902	0.360	1.64	1.58
	MRD-CI^b	2.8155	1781	56	7.7803	0.392		1.60
A$^2\Delta$	H^v	2.9110	1581.2	155.7	7.204	0.546	0.875	3.55
	MRD-CI^b	2.9225	1458	60	7.2224	0.415		3.40
	exptl^c	2.9718 (R$_o$)	1398.8		6.9833			3.25

^{a}Ref. 49, ^{b}Ref. 45, ^{c}Ref. 59.

dissociation channel of P$^+$(^{1}D)+H(^{2}S).

The specrtroscopic constants for the bound PH valence states are listed in Table 9. The equilibrium internuclear distance calculated by using second order H^v are found to be in reasonable agreement with experimetnal[52,56-58] and theoretical[37,45] values. Since the X$^3\Sigma^-$, a$^1\Delta$ and b$^1\Sigma^+$ states are parallel to each other, this situation is relflected in the similar values of the various spectroscopic constants. The A$^3\Pi$ state is found to be slightly bound. Therefore in our calculation potential energy curve for the A$^3\Pi$ state leads to T$_e$ value of 4.06 eV, which is higher by 0.4 eV than the corresponding experimental data.[52,56,57]

The various spectroscopic constants for the low-lying bound states of PH$^+$ are listed in Table 10. The frequency assigned to the X$^2\Pi$ state has slightly larger deviation from the experimental[59] and other theoretical[45,49] data. In $^4\Sigma^-$ and A$^2\Delta$ states, the increase of the equilibrium bond length is also consistent with the low vibrational frequencies and an increase in the anharmonicity constants going from the X$^2\Pi$ state to the $^4\Sigma^-$ and to the A$^2\Delta$ states.

Conclusions

The ab initio effective valence shell Hamiltonian has been applied to second row diatomic hydrides, e.g., SiH and PH. Whole computations are performed using the second order expansion form of energy independent H^v formalism with a triple zeta plus polarization quality basis set. This work is the first application of effective Hamiltonian theory to hydrides containing second row elements.

The H^v calculated valence state energies of SiH, SiH$^+$, PH, and PH$^+$ are in good agreement with those from other extensive CI calculations. It confirms that the second order H^v computes correlation energies properly. Furthermore, a single computation of H^v matrix elements describes valence states of a molecule and its ion simultaneously. It signifies the fact that the H^v is a good ab initio method to generate all the valence states with same chemical accuracy regardless of their charge states.

As mentioned before, the H^v matrix elements are effective integrals between valence molecular orbitals. With these matrix elements alone we have successfully reproduce all the

valence state energies. It implies that these matrix elements must be so called "parameters" used in semiempirical theories. Then how are H^v matrix elements related to semiempirical parameters? It is a very important question. The reason why we have been applying the effective valence shell Hamiltonian to various systems is to find an answer to the above question although many reliable ab initio methods already exist. A study on this problem is currently under way.

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