

Adiabatic and quasidiabatic $2\Sigma^+$ states of BeH

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An approach to the calculation of quasidiabatic states is presented and applied to the rather entangled spectrum of the first five BeH $2\Sigma^+$ excited states. The method of transformation from the adiabatic to the diabatic description employs a criterion of maximum nonorthonormal overlap between sequential diabatic states along the coordinate of interest, starting with the dissociation region as a reference point. The computational method is general and capable of separating out diabatic states from a set of adiabatic ones of mixed character, involving valence, Rydberg and ion-pair contributions.

I. INTRODUCTION

The subject of defining and computing accurate diabatic or quasidiabatic states is of continuing interest and importance [e.g., Refs. 1 and 2 and References therein]. The conventional method for obtaining (formally) such states is to perform suitable transformations on the complete set of accurately computed adiabatic states.^{3,4} However, this requires the use of matrix elements of $\partial/\partial Q$ -type operators (Q is an appropriate coordinate) between adiabatic states, whose efficient and reliable computation is known to be very cumbersome and uncertain in regions of avoided or conical intersections. Therefore, it is important to develop and test methods which either construct diabatic states directly or utilize accurate adiabatic wave functions but not matrix elements of $\partial/\partial Q$. Such approaches can be found in Refs. 2,5–14.

In this paper we present a method for the construction of quasidiabatic states without computing $\partial/\partial Q$ matrix elements and demonstrate its potential on the $2\Sigma^+$ spectrum of BeH. The method was first applied to the Rydberg states of HeH (Ref. 2) whose structure is relatively simple. Now, the case of BeH is more demanding due to the existence of near-degeneracy effects and low-lying states of Be. Strong nonadiabatic interactions between the electronic states of BeH have been found in previous theoretical^{15–17} and spectroscopic work.^{18,19} In particular, the first excited $2\Sigma^+$ state, $C^2\Sigma^+$, which has a minimum at large internuclear distances, predissociates the higher lying Rydberg states of BeH.^{16–19} Thus the diabatic description might prove to be more appropriate for this system. A previous drawing of diabatic potentials of BeH was based on the population of the orbitals characterizing the states.¹⁷

II. BACKGROUND AND PRESENT COMPUTATIONAL METHOD

Our approach implements the following ideas. We remind ourselves that the diabatic states correspond to effective (projected) Hamiltonians whose construction depends on the geometry-dependent function space defining them.^{5,6} An important element in choosing this function space is the existence of a physically clearcut reference point, and this is the dissociation region.⁶ In this region,

where the diabatic states coincide with the adiabatic ones, one may create reference states, which are properly correlated by the inclusion of the important state-specific near-degeneracy correlation effects.⁶ Having done this, the purpose of the essential calculation is to be able to stepwise propagate the desired solution along the chemically important coordinate. This can be done by imposing on the geometry-dependent sequential solutions constraints such as projecting out electronic structure-derived Hartree-Fock orbitals⁶ or maximization of overlap at each step of the calculation with the previous solution, starting with the function space defined by the asymptotic reference states.^{9,10,14}

Following and expanding on the above, the first step involves a calculation of a number of N adiabatic states (Ψ_k) at a geometry (geometry 1) in the asymptotic region. The diabatic states (D_k) at this geometry are chosen to coincide with the adiabatic, i.e.,

$$D_k^1 = \Psi_k^1 \quad (k=1, \dots, N). \quad (1)$$

The choice of the initial geometry is rather crucial, since it is the character of the k th adiabatic state at geometry 1 which shall determine the k th diabatic state.

Given a set of N adiabatic states at a geometry 2, the k th diabatic state $D_k^{(2)}$ is obtained as

$$D_k^{(2)} = \sum_i^N c_{ki}^{(2)} \Psi_i^{(2)}, \quad (2)$$

where the coefficients $c_{ki}^{(2)}$ are determined by maximization of the overlap $\langle D_k^{(1)} | D_k^{(2)} \rangle$ under the constraint that $D_k^{(2)}$ is normalized to unity. This is equivalent to maximization of the quantity

$$X = \left| \left\langle \sum_i c_{ki}^{(2)} \Psi_i^{(2)} \middle| D_k^{(1)} \right\rangle \right|^2 - \omega \left\langle \sum_i c_{ki}^{(2)} \Psi_i^{(2)} \middle| \sum_j c_{kj}^{(2)} \Psi_j^{(2)} \right\rangle, \quad (3)$$

where ω is a Lagrange multiplier.

The requirement $\partial x / \partial c_{ki} = 0$ leads to the diagonalization of a matrix S^k given by

$$S_{ij}^k = \langle D_k^{(1)} | \Psi_i^{(2)} \rangle \langle D_k^{(1)} | \Psi_j^{(2)} \rangle. \quad (4)$$

The k th diabatic state at geometry 2, $D_k^{(2)}$, is given by the eigenfunction of S^k corresponding to the largest eigenvalue. If $k > 1$, it is necessary to orthogonalize $D_k^{(2)}$ to the $D_1^{(2)}, \dots, D_{k-1}^{(2)}$ diabatic states. This is accomplished by Schmidt orthogonalization which preserves the notion of ordering of the states in terms of ground and successive excited states. The diabatic states thus determined for geometry 2 may be employed as reference for a calculation at a subsequent geometry.

At any geometry n , the electronic Hamiltonian matrix $E^{(n)}$ in the basis of diabatic states has elements

$$E_{kl}^{(n)} = \langle D_k^{(n)} | H | D_l^{(n)} \rangle = \sum_i c_{ki}^{(n)} c_{li}^{(n)} \langle \Psi_i^{(n)} | H | \Psi_i^{(n)} \rangle. \quad (5)$$

The diagonal matrix elements of E give the diabatic potentials, while the off-diagonal (or interaction) matrix elements may be employed for calculations of rates of transitions between the diabatic states. Diagonalization of this matrix E gives back the adiabatic energies.

Since, in general, the reference states $D_k^{(n-1)}$ are linear combinations of adiabatic wave functions, the calculation of the S^k matrices [cf. Eq. (3)] requires calculation of nonorthonormal (NON) overlaps,

$$\langle \Psi_m^{(n-1)} | \Psi_l^{(n)} \rangle \quad \text{for } m=1, \dots, N \quad \text{and } l=1, \dots, N \quad (6)$$

between adiabatic wave functions calculated at two different geometries, $n-1$ and n . Given an AO basis set, the character of a CI wave function is specified by the character of the molecular orbitals and the coefficients of the CI expansion. Thus in the present method, only the changes in the MO and in the CI coefficients are taken into account, while the translation of the atomic orbitals between the two geometries is neglected in the sense that only the AO overlap integrals of the current (n) geometry are employed. Gadéa and Pélissier¹⁴ employ a modified overlap matrix over the AO, whereby the upper triangle involves the reference and the lower the current geometries.

The adiabatic functions are linear combinations of determinants, $\{\Delta_j^{(n)}\}$. Hence, the overlaps (6) are reduced to overlaps over determinants which are given by

$$\langle \Delta_i^{(n-1)} | \Delta_j^{(n)} \rangle = \det(\mathbf{D}^{IJ}) \quad (7)$$

with

$$\mathbf{D}_{ij}^{IJ} = \langle \varphi_{ii}^{(n-1)} | \varphi_{jj}^{(n)} \rangle. \quad (8)$$

It should be noted that all the adiabatic states at a given geometry are obtained from the same CI calculations which means that they are constructed from a common set of determinants. Thus calculation of the NON overlaps over determinants [Eq. (7)] is required only once although, in general, N -electron overlap integrals [Eq. (6)] need to be determined. These NON overlaps are computed by the methods and programs already developed^{21,22} for the study of molecular properties within the framework of state-specific theory.²³

III. DETAILS OF THE CALCULATIONS

Adiabatic potential energy curves were calculated for eleven electronic states of BeH, six ${}^2\Sigma^+$, four ${}^2\Pi$ and one ${}^2\Delta$. Although the present work deals mostly with the ${}^2\Sigma^+$ states of BeH, future work will be devoted to those of ${}^2\Pi$ symmetry. The AO basis set which was employed for the calculations is as follows: For hydrogen the (6s/4s) basis set of Huzinaga²⁰ was augmented with two p polarization functions with exponents 0.7 and 0.2, respectively, and one s and one p Rydberg functions with exponents 0.025 and 0.035, respectively. For beryllium, the (10s/12s) basis of Dunning²⁴ was augmented with the (5p/3p) basis from Dykstra *et al.*,²⁵ one d polarization function with exponent 0.32, two s , two p , and two d Rydberg functions with exponents obtained by splitting the exponent 0.015 after Dunning and Hay²⁶ two more Rydberg s functions obtained by splitting the exponent 0.003 by the factors 1.9 and 0.75,²⁶ and finally one further Rydberg p function with exponent 0.003. This Rydberg basis set should be sufficient for the calculation of Rydberg states up to $4p$.

The calculations have been carried out with the MRD-CI programs^{27,28} in C_{2v} symmetry. Thus the first six 2A_1 states (five ${}^2\Sigma^+$ and one ${}^2\Delta$ for internuclear distances from 1.0 to 4.0 bohr, but six ${}^2\Sigma^+$ from 4.5 to 20.0 bohr) and the first four 2B_1 (${}^2\Pi$) have been calculated for values of the internuclear distance R from 1.0 to 20.0 bohr. For the 2A_1 calculations, a reference set of 91 configuration functions and an energy threshold^{27,28} of 1 μH was employed. The resulting selected CI spaces varied between 10 000 and 3000 configurations for the short and the very long R region, respectively. The corresponding data for the 2B_1 states is 51 reference configurations, 1 μH threshold and from 10 000 to 7500 configuration functions for short and long R , respectively.

Vibrational calculations were carried out on the first three electronic states with the aid of analytic methods²⁹ employing series of trigonometric functions for the fitting of the potentials and of basis sets.

IV. RESULTS AND DISCUSSION

A. Adiabatic states

The adiabatic electronic energies of the various states of BeH are plotted in Fig. 1, where the dotted line corresponds to the ${}^2\Delta$ state for $1.0 < R < 4.0$ bohr, while for $R > 4.0$ bohr it gives the $6{}^2\Sigma^+$ state.

A comparison of Fig. 1 with the corresponding figures of Henriët and Verhaegen¹⁷ shows that there is close agreement of the two sets of results, except for the slightly lower overall energies obtained in the present work.

The potential energy curves of the higher lying electronic states of BeH (see Fig. 1 and for the ${}^2\Sigma^+$ states also Fig. 2), show a number of avoided crossings. They exhibit deep minima at about 2.5 bohr, characteristic of Rydberg states [r_e of BeH^+ being 2.48 bohr (Ref. 30)], but it is clear that at short R they are perturbed and predissociated by the $C{}^2\Sigma^+$ state, to an extent depending on the particular state. There is no experimental observation of the $3{}^2\Sigma^+$ and $4{}^2\Sigma^+$ states, while $5{}^2\Sigma^+$ may contribute to observa-

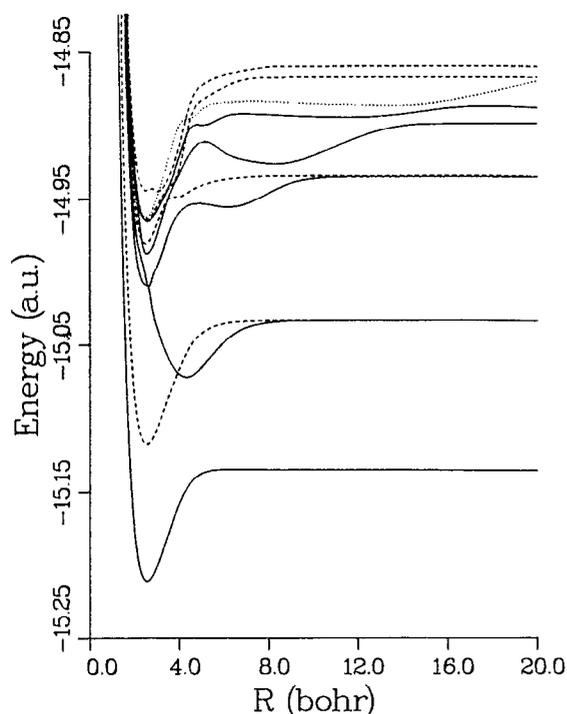


FIG. 1. Adiabatic potential energy curves for $X^2\Sigma^+$, $C^2\Sigma^+$, $3^2\Sigma^+$, $4^2\Sigma^+$, and $5^2\Sigma^+$ (solid lines), $B^2\Pi$, $2^2\Pi$, $3^2\Pi$, and $4^2\Pi$ (dashed lines) and $1^2\Delta$ state of BeH (dotted line).

tions of the D state¹⁸ of BeH. At R of around 3.0 bohr, a series of avoided crossings are shown, reflecting interactions between states of $H+Be^*$ character with those of H^++Be character. In addition, at an internuclear distance of 6.0 bohr, a (Be^++H^-) ion-pair contribution appears in the wave function of $3^2\Sigma^+$ and contributes to the character of successive states as R increases out to 20.0 bohr, where it contributes mostly to the $6^2\Sigma^+$ state.

Although the adiabatic states of BeH are not of main concern in this work, a comparison of theoretical quantities with corresponding experimental data may aid in the estimation of the accuracy of the adiabatic calculations. In

TABLE I. Vertical theoretical transition energies (eV) at $R=2.54$ bohr, with respect to the ground state, and comparison with experimental T_e values (Refs. 18, 19).

State	ΔE (eV)	T_e (eV)
$X^2\Sigma^+$	0.00	0.00
$A^2\Pi$	2.56	2.48
$C^2\Sigma^+$	5.51, 3.77 ^a	3.83
$3^2\Sigma^+$	5.61	...
$4^2\Sigma^+$	6.12	6.06 ^b
$B^2\Pi$	6.31	6.31
$5^2\Sigma^+$	6.71	...
$3^2\Pi$	6.74	6.70
$1^2\Delta$	6.77	...
$4^2\Pi$	7.27	7.28

^aTheoretical T_e value.

^bExperimental value estimated in Refs. 16 and 18.

Table I, vertical transition energies of the excited states from the ground state at R of 2.54 bohr are listed along with experimental T_e values.^{18,19} As shown, the theoretical ΔE (T_e for $C^2\Sigma^+$) are within 0.08 eV of the experimental T_e values when such are available.

In Table II, some quantities obtained from vibrational calculations on the potentials of the $X^2\Sigma^+$, $C^2\Sigma^+$, and $1^2\Pi$ states for BeH and BeD are listed, along with the corresponding experimental data^{18,19} in brackets. The agreement of the theoretical results with the experimental data is quite good.

B. Quasidiabatic states

The adiabatic potentials of the excited $^2\Sigma^+$ states calculated in the present work are shown in Fig. 2. The $6^2\Sigma^+$ state has been calculated only for $R > 4.0$ bohr since at shorter R the sixth 2A_1 root corresponds to the $1^2\Delta$ Rydberg state of BeH.

As shown in Fig. 2, the interaction of the $C^2\Sigma^+$ and $3^2\Sigma^+$ states at short R is rather obvious and is manifested by the sharp avoided crossing of the two potentials. However, at larger R , it is not possible to infer diabatic potentials on the basis of the avoided crossings. It is therefore

TABLE II. Spectroscopic constants (cm^{-1})^a for the first three electronic states of BeH and BeD.

State/system	R_e (Å)	ω_e	$\omega_e X_e$	B_e	D_e^c (eV)
$X^2\Sigma^+$ /BeH	1.3457	2049	40.1	10.266	2.077
	(1.3426)	(2060.78)	(36.31)	(10.3164)	(2.16) ^b
$X^2\Sigma^+$ /BeD	1.3457	1521	22.5	5.65	2.077
	(1.3419)	(1530.32)	(20.71)	(5.6872)	...
$A^2\Pi$ /BeH	1.3377	2079	46.2	10.39	2.268
	(1.3335)	(2088.58)	(40.14)	(10.4567)	...
$A^2\Pi$ /BeD	1.3377	1545	26.2	5.72	2.268
	(1.3331)	(1551.13)	(23.00)	(5.7614)	...
$C^2\Sigma^+$ /BeH	2.3066	1053	31.4	3.496	1.050
	(2.301)	(1061.12)	(42.19)	(3.5141)	(1.048) ^b
$C^2\Sigma^+$ /BeD	2.3066	787	18.7	1.93	1.050
	...	(787.40)	(23.23)	(1.9367)	...

^aValues in brackets are experimental, from Ref. 18.

^bExperimental values from Ref. 19.

^cDissociation energy.

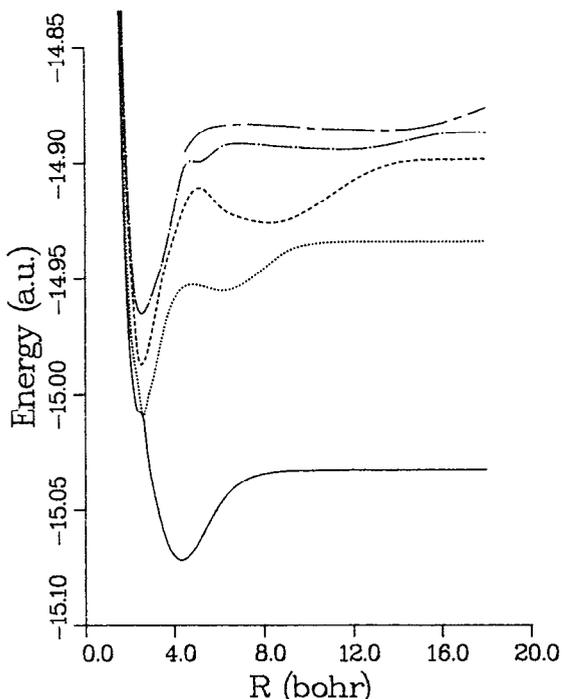


FIG. 2. Adiabatic potential energy curves for the first five excited ${}^2\Sigma^+$ states of BeH.

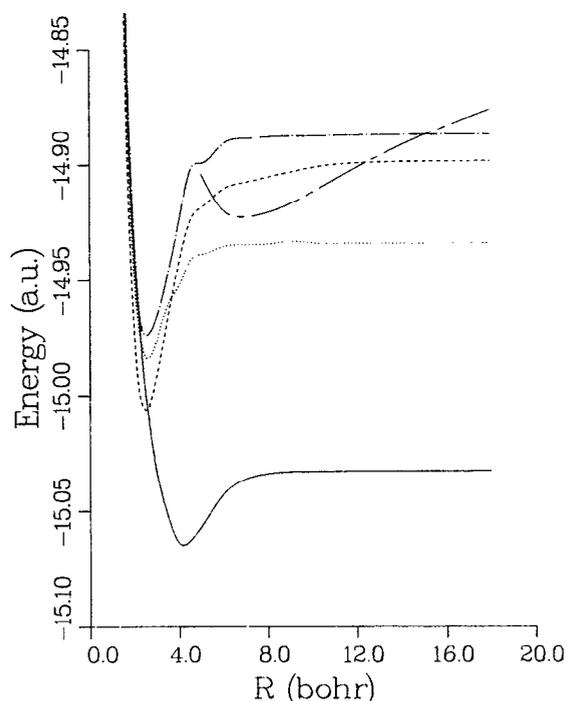


FIG. 3. Diabatic potential energy curves for the first five excited ${}^2\Sigma^+$ states of BeH.

necessary to apply a more quantitative and systematic approach, such as that described in Sec. II. The main objective of this work was to obtain a description of the interaction of the $C^2\Sigma^+$, $3^2\Sigma^+$, $4^2\Sigma^+$, and $5^2\Sigma^+$ states in terms of diabatic potentials. Hence, the adiabatic basis must include the above four states. A consideration of Fig. 2 shows that a 4×4 calculation might be sufficient for the region around the potential well. However, for $R > 4.0$ bohr it is necessary to include the $6^2\Sigma^+$ state as it interacts with the lower states (cf. Fig. 2). The starting point of the calculation of the diabatic states is at R of 20.0 bohr. At this distance the ${}^2\Sigma^+$ states have not yet attained the character of the corresponding states of the separated atoms (as also noted by Henriët and Verhaegen¹⁷ for $R = 16.0$ bohr). The character of the states at 20.0 bohr is Rydberg, except for $6^2\Sigma^+$ which is mainly ion pair. The $C^2\Sigma^+$ state has mixed valence and Rydberg character, while the $3^2\Sigma^+$, $4^2\Sigma^+$, and $5^2\Sigma^+$ states have Rydberg contributions from all three atomic symmetries s , p , and d .

The adiabatic states calculated at 20.0 bohr serve as the reference diabatic state for the next shorter R point, at 18.0 bohr. The calculations proceed stepwise with a step of 2.0 bohr down to $R = 10.0$ bohr, a step 1.0 from 10.0 to 5.0, a step of 0.5 until $R = 3.0$ bohr and steps of 0.2 and 0.1 for shorter R values down to 1.0 bohr.

The resulting diabatic potentials are plotted in Fig. 3 and also in Fig. 4, where an enlargement of the short R region is given. The corresponding interaction matrix elements [E_{ij} of Eq. (5)] are all small, of maximum magnitude under 0.025 hartree.

As shown in Figs. 3 and 4, the diabatic $C^2\Sigma^+$ intersects the potentials of the $3^2\Sigma^+$ and $4^2\Sigma^+$ states, but not of the $5^2\Sigma^+$. A comparison of the adiabatic potentials, (Fig. 2), with the diabatic ones, (Fig. 3), shows that most of the structure in the first set has been smoothed out in the second one. An interesting feature of the large R region is the appearance of the diabatic ion-pair state, which is the highest state at 20.0 bohr, dips and crosses the next two lower Rydberg states at shorter R , acquires a broad minimum around 7.0 bohr and rises sharply at shorter R . It was not possible to generate this state at $R < 4.0$ bohr in the basis of adiabatic functions considered. It must be noted that all five adiabatic states must be included in the calculation in order to obtain the results of Fig. 3. If only four adiabatic states are considered, the resulting diabatic potentials (see Fig. 5) are not smooth but indicate the presence of further interactions, while the ion-pair state cannot be resolved. While the main interactions have been disentangled in the 5×5 calculation (Figs. 3 and 4), some remaining wavy structure at large R indicates the need for an even larger adiabatic basis set. Similarly, although, as noted above, the diabatic curves of $C^2\Sigma^+$ and $5^2\Sigma^+$ do not cross (cf. Fig. 4) it is conceivable that inclusion of even higher adiabatic states might alter this picture. Since a truncated set of adiabatic states is employed, at some point it may not be sufficient for the higher diabatic states. It is thus a question of selection of the appropriate basis set for a given problem of interest.

The above results show that, in general, it is not possible to guess the diabatic potentials on the basis of the

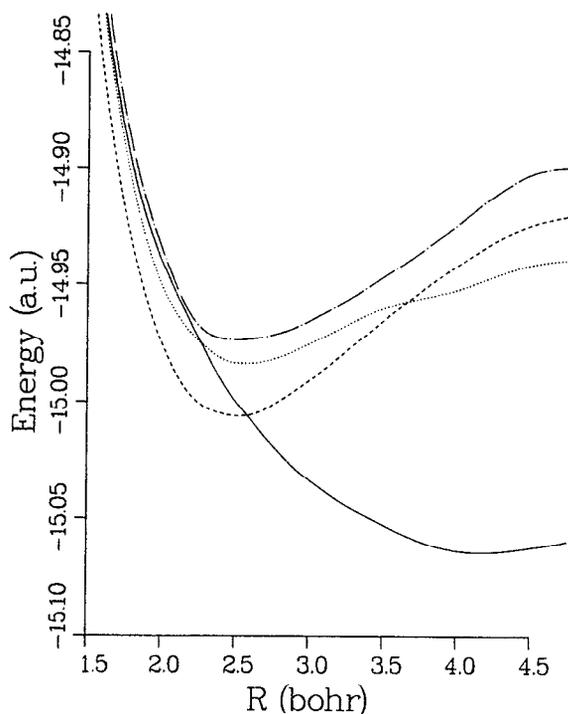


FIG. 4. As in Fig. 4, but closeup of the short R region.

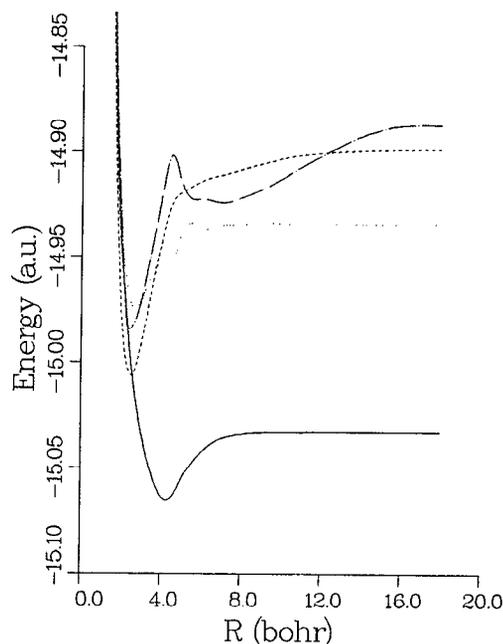


FIG. 5. Diabatic potential energy curves for the first four ${}^2\Sigma^+$ states resulting from a 4×4 treatment. As explained in the text, this treatment is inadequate.

avoided crossings of the adiabatic but a more quantitative approach is required. The present method is capable of producing diabatic states (potentials and wave functions) of different types, provided that the adiabatic basis is sufficient. The applications of the method thus far have involved diatomic systems where, at least in principle, it is possible to compute radial coupling matrix elements and transform to diabatic states. Applications to polyatomic molecules where strict diabaticization is not possible, should reveal the power along with possible shortcomings of the method better. Such applications shall be the subject of future work.

V. CONCLUSION

Spectroscopic and previous theoretical work on BeH shows that the electronic states of BeH have rather complicated potential energy curves, with many interactions. As the electronic states of BeH have mixtures of Rydberg, valence, and ion-pair character, it is rather difficult to decide on the character of the corresponding diabatic potentials. The method discussed here has been successful in unraveling the structure in the adiabatic potential. At short R this is due to the interaction of the Rydberg states with the valence $C^2\Sigma^+$ state, while at long R it is mostly due to the interaction of the Rydberg states with an ion-pair state.

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