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Nonadiabatic generator-coordinate calculation of H_2^+

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We report on a nonadiabatic calculation of the few lowest $J=0$ states in the H_2^+ molecule done within the framework of the generator-coordinate method. Substantial accuracy is achieved with the diagonalization of matrices of very modest dimensions. The resulting wave functions are strongly dominated by just a few basis states. The computational scheme is set up so as to take the best advantage of good analytical approximations to existing adiabatic molecular wave functions.

I. INTRODUCTION

The generator-coordinate method[1] (GCM) is a variational method largely employed in nuclear physics in the last twenty years.[2] It is now beginning to be applied to atomic and molecular systems.[3–7] Owing to the generality of the method, moreover, many calculations exist that can be interpreted as "unconscious" applications of the GCM, see, for instance, Ref. 8. The purpose of this work is to report on an exploratory calculation of some low-lying $J=0$ states of the H_2^+ molecule with the use of the GCM in a way that allows for nonadiabatic couplings to become operative. We will, in particular, set up the method in such a way as to able to take maximum advantage of good analytical approximations to the adiabatic wave function for the same molecule.

The trial wave function of the GCM is typically written as a linear superposition of a continuous family of labeled functions $\phi(\alpha)$, where the labels α are called the generator coordinates. They span a purely technical space—the label space[9]—and are, in fact, integrated out in the typical GCM ansatz for the trial wave function:

$$\Psi=\int d\alpha\, f(\alpha)\phi(\alpha) \tag{1.1}$$

in which $f(\alpha)$ is a weight function for the linear superposition defining Ψ, to be determined variationally. The optimal weight functions $f(\alpha)$ are found to satisfy the integral equation named after Hill, Wheeler, and Griffin:

$$\int d\alpha'[H(\alpha,\alpha')-ES(\alpha,\alpha')]f(\alpha')=0\ , \tag{1.2}$$

where

$$H(\alpha,\alpha')=\langle\phi(\alpha)\,|\,H\,|\,\phi(\alpha')\rangle$$

and

$$S(\alpha,\alpha')=\langle\phi(\alpha)\,|\,\phi(\alpha')\rangle$$

are, respectively, the energy and overlap kernels. H is the full Hamiltonian of the system under consideration.

Analytical solutions of Eq. (1.2) are possible only for rather special systems, and, in general, one resorts to numerical techniques involving a discretized version of this equation. The discretization techniques currently used are reviewed in Sec. II below. In Sec. III we review some relevant calculations of H_2^+ and then describe an exploratory application of the GCM to this simple system in Secs. IV–VI. Section VII contains some concluding remarks.

II. THE DISCRETIZED GCM

In numerical applications one usually replaces Eq. (1.1) by (see, e.g., Ref. 6)

$$\Psi=\sum_i c_i\phi(\alpha_i)\ , \tag{2.1}$$

where the sum runs over the points α_i of some given mesh in label space. While it is possible to take Eq. (2.1) to be a discrete approximation to the integral (1.1), it is also possible, in view of the general variational character of the method, to treat it as a proposed ansatz in which the weights c_i and/or the mesh points α_i are to be determined variationally. In this latter case, the main relation to the continuous GCM resides in writing the ansatz as a superposition of a given parametrized basis function $\phi(\alpha)$ with itself (at different parameter values), rather than with other (possibly orthogonal) functions, as done, e.g., in configuration-interaction calculations. Given a mesh $\{\alpha_i\}$ in label space, the optimal weights c_i are found in the standard way to satisfy the discretized version of Eq. (2.1), i.e.,

$$\sum_j (H_{ij}-E_nS_{ij})c_j^{(n)}=0\ , \tag{2.2}$$

where $H_{ij}=H(\alpha_i,\alpha_j)$ and a similar notation is used for S_{ij}. Leaving aside any reference to the GCM, Eq. (2.2) can be immediately linked to a well known quantum-chemical methodology: for the given basis [this is a nonorthogonal basis formed by the $\phi(\alpha_i)$ evaluated at the chosen mesh points in label space] the coefficients $c_j^{(n)}$ are the optimal linear variational coefficients. With them, as many values of E are obtained as there are meshpoints (or, more generally, as there are linearly independent vectors in the adopted basis). These will be variational upper bounds for the same number of lower exact eigenvalues of H.[10]

The quality of the results obtained by using Eqs. (2.1) and (2.2) to approximate variationally the stationary states of a given (molecular) system, on the other hand, will clearly depend (i) on the particular form chosen for the parametrized wave function $\phi(\alpha)$ and (ii) on the particular set of mesh points adopted to set up Eq. (2.1). We assume, of course, the system to be characterized dynamically by its Hamiltonian H, expressed in terms of a complete set of dynamical variables acting in $\phi(\alpha)$.

Deferring the discussion of point (i) to Sec. IV, we may note, concerning point (ii), that there are at least four distinct procedures for selecting the meshpoints $\{\alpha_i\}$ which can be recognized in the literature[6].

(A) Adopt a large number of mesh points, separated by equal spacings $\Delta\alpha$ or by some other "*a priori*" prescription, around the single variational optimum α_0 which minimizes

$$E(\alpha)=H(\alpha,\alpha)/S(\alpha,\alpha)$$

(Ref. 8).

(B) Select the $\{\alpha_i\}$ on the basis of some quadrature rule.[3]

(C) Select the $\{\alpha_i\}$ by the iterative method proposed by Caurier[2]: Given a sequence $(\alpha_1,\ldots,\alpha_{n-1})$, choose α_n to minimize the lowest energy eigenvalues in Eq. (2.2) (see also Ref. 6).

(D) Adopt a "brute-force" optimization procedure treating all nonlinear parameters α_i as variational parameters.[11]

In any one of such procedures (and, in fact, in connection with the continuous GCM as well, see Ref. 9) due care should be taken with an important technical difficulty due to the nonorthogonality of the basis $\{\phi(\alpha_i)\}$: increasing the number of mesh points and/or decreasing the separation between mesh points will lead, from a certain point on, to an approximate linear dependence (ALD) of the basis that will enhance numerical noise. Following Ref. 12, we may characterize such ALD by the criterion that the ratio of the largest to the smallest eigenvalue of the overlap matrix S_{ij} is larger than 10^N, where N is the number of decimal figures carried in the calculations. One particular consequence of the onset of ALD is that the upper bound variational property of the energy will be progressively obfuscated by numerical inaccuracies.

The ALD tends to make the overlap matrix nearly singular. Thus the solution of the eigenvalue problem (2.2) can no longer be safely carried out by traditional matrix inversion methods. In order to bypass this difficulty, an alternative scheme is frequently used in connection with generator-coordinate (GC) calculation which can be summarized as follows.[13]

(i) Diagonalize the matrix S_{ij}, i.e., obtain λ_k and $\{b_i^k\}$ such that

$$\sum_j S_{ij}b_j^k=\lambda_k b_i^k \;.$$

(ii) Form the orthonormal set of vectors

$$\tilde{\phi}_k=\sum_i \frac{b_i^k}{\sqrt{\lambda_k}}\phi(\alpha_i) \;. \tag{2.3}$$

They provide for an alternate orthonormal basis in which the Hamiltonian matrix appears, in terms of H_{ij}, as

$$\tilde{H}_{kl}=\sum_{ij}\frac{b_i^{k*}}{\sqrt{\lambda_k}}H_{ij}\frac{b_j^k}{\sqrt{\lambda_l}} \tag{2.4}$$

which makes the source of trouble apparent through the occurrence of terms in the sum with vanishingly small denominators (the small eigenvalues of the overlap matrix), thus the following.

(iii) Truncate the Hamiltonian matrix (2.4) by eliminating all eigenvectors $\tilde{\phi}_k$ associated with eigenvalues λ_k of S_{ij} smaller than a suitable limit θ. This truncation scheme amounts to removing from the original nonorthogonal basis independent components of nearly zero norm. The solution of Eq. (2.2) is then replaced by the diagonalization of the truncated version of Eq. (2.4). In favorable cases, the discarded vectors do not contribute appreciably to the eigenstates of $\tilde{H}_{kl}$ with the lowest eigenvalues, while still being able to generate unwanted numerical noise if carried in the calculation.

III. H_2^+ CALCULATIONS: A SURVEY

A. Discretized GC adiabatic calculations

We mention here three electronic variational GC calculations for H_2^+ which, however, make no explicit reference to the GCM.[11,14,15] The first of these (Ref. 11) makes use of procedure (D) (see Sec. II) for selecting nine values of each one of two generator coordinates, and performs, in addition, the usual determinantal optimization of nine linear coefficients. It leads to an excellent value for the ground-state energy. The chosen generating function $\phi(\alpha)$ is a simple Gaussian.

B. Nonadiabatic calculations

1. Variational calculations

An early calculation by Froman and Kinsey[16] does not achieve accuracy up to the third decimal figure for the ground-state energy of H_2^+. Curiously, these authors have detected problems with ALD (their basis was not orthogonal).

A series of three variational calculations in the preceding decade have led to the best known results for the first "vibrational" ($J=0$) energies of H_2^+.[17–19] The basis set is formed by the functions[18]

$$\phi_{\mu\nu n}(\epsilon,\eta,R)=\epsilon^{\nu}e^{-\alpha\epsilon}\eta^{\mu}\cosh(\beta\eta)R^{-3/2}\times\exp\left[-\frac{\gamma^2}{2}(R-\delta)^2\right]H_n(R-\delta) \;, \tag{3.1}$$

where ϵ and η are two electronic coordinates in confocal elliptical coordinates and R is the internuclear distance. These functions involve four nonlinear variational parameters α, β, γ, and δ, and $H_n(R-\delta)$ are Hermite polynomials. The value of the ground-state energy obtained in Ref. 17 with an expression involving 57 terms is $-0.597\,1387$ a.u. (the best adiabatic value being $-0.597\,1385$ a.u., see Ref. 18). An expansion involving 176 terms yielded the value $-0.597\,139\,05$ a.u. (Ref. 18) and, when pushed to nearly 500 terms, the value $-0.597\,139\,06$ a.u. (Ref. 19).

2. *Perturbation calculations*

The nonadiabatic variational calculations described above have not, until now, taken full advantage of the information contained in exact adiabatic wave functions, or in good approximations for them. If, in fact, one takes the leading term of the basis (3.1) [i.e., $\phi_{000}(\epsilon,\eta,R)$], and takes for the four nonlinear parameters the values of Ref. 18 (optimized for the entire expansion), the resulting ground-state energy is very poor. In 1967 Hunter and Pritchard[20] were able to obtain the value $-0.597\,138\,7$ a.u. adopting a perturbation treatment starting from the adiabatic ground-state wave function and mixing in two adiabatic excited states. Further improvement along these lines was, however, hard to obtain. In 1978, Wolniewicz and Pohl[21] were able to obtain the value $-0.597\,139\,05$ a.u. in a combined variational-perturbation calculation which still needed many term expansions. Energies obtained in this calculation for the first two vibrational excitations were also less accurate than those obtained in Ref. 19.

No GC-type nonadiabatic calculations appear to be availabe to date for $H_2{}^+$.

IV. NONADIABATIC GC CALCULATION FOR $H_2{}^+$

Why should one attempt another nonadiabatic calculation for $H_2{}^+$? An answer to this question contains the main motivation for the present work: a GC calculation may allow for the possibility of taking maximum advantage of the information already contained in good analytical approximations to adiabatic wave functions in terms of the simplest and most widespread method in quantum chemistry, viz., the variational method. Particularly in ground "electronic" state calculations, one needs just a good variational adiabatic wave function for the lowest eigenstate (a $J=0$, $v=0$ state), $\phi_0^{\mathrm{ad}}=\varphi_0^{\mathrm{el}}X^{\mathrm{nuc}}$. One is freed from the requirement of including excited electronic states in order to allow for nonadiabaticity, since nondiagonal matrix elements $H(\alpha,\alpha')$ involving wave functions of the same analytical form ϕ_0^{ad} actually allow for the incorporation of nonadiabatic couplings.[7] An additional, technical advantage should also be mentioned: since the GC basis set $\{\phi_0^{\mathrm{ad}}(\alpha_i)\}$ involves elements of the same analytical form, the energy matrix $H(\alpha_i,\alpha_j)$ is given in terms of one single analytical expression. A similar statement also holds, of course, for the overlap matrix $S(\alpha_i,\alpha_j)$.

A. Choosing the generating function $\phi(\alpha)$

We restrict ourselves in this work to rotationally invariant, (i.e., $J=0$) eigenstates. This restriction is implemented, as usual, by projecting the complete Hamiltonian onto the $J=0$ subspace. This is conveniently done in the coordinate system of Ref. 22, which contains three variables: two electron-nucleus distances, r_A and r_B, and the internuclear distance R. The generating function will, therefore, also involve only these three variables. For the present exploratory calculation we have chosen as a generating function the adiabatic wave function[22]

$$\begin{aligned}\phi(\alpha,\beta,\delta)&=\varphi_{\mathrm{GZ}}(r_A,r_B;\alpha,\beta)X(R,\delta)\\&=\exp[-\alpha(r_A+r_B)]2\cosh[\beta(r_A-r_B)]\\&\quad\times\exp\left[-\frac{\gamma^2}{2}(R-\delta)^2\right].\end{aligned}\tag{4.1}$$

The electronic factor φ_{GZ} is the Guillemin-Zener wave function.[23] Optimal variational values for α, β, γ, and δ, determined by Diehl and Flügge,[22] are

$$\begin{aligned}&\alpha_0=1.346,\quad \beta_0=0.913\ ,\\&\gamma_0=3.200,\quad \delta_0=2.043\ ,\end{aligned}\tag{4.2}$$

leading to the value $-0.596\,430$ a.u. for the ground-state energy.

We have selected α, β, and δ as generator coordinates. The parameter γ was held fixed at its optimum variational value γ_0. The expansion (2.1) is, therefore, now written as

$$\psi=\sum_{\alpha,\beta,\delta}c_{\alpha\beta\delta}\phi(\alpha,\beta,\delta)\ ,\tag{4.3}$$

where the sum runs over the adopted mesh points. The choice of these is discussed in Sec. IV B. Actually, it can be shown[9] that were one to treat δ as an unrestricted, continuous generator coordinate, this amounts to no restriction regarding the internuclear degree of freedom R. A great deal of flexibility is to be expected by allowing for the coupling of these generator coordinates. Particularly, dynamical couplings involving δ and the electronic generator coordinates α and β will introduce dynamical correlations between nuclear and electronic motion.[7]

It should be noted also that the symmetry of the electronic part of (4.1) does not allow for bound electronic excitations of the molecule. Thus, the number of bound states obtainable from the secular determinant will always be limited by the number of different values of δ. They can be associated essentially with nuclear vibrational excitations.

B. Choosing the GC mesh points

We have adopted procedure (A) (see Sec. II), in its simplest form, for selecting the GC mesh points: A fixed interval was chosen for each one of the three generator coordinates, and a variable number of points were used in the neighborhood of the variationally optimal values given in (4.2). Moreover, it has been found useful to carry out the following two types of preliminary probing tests before attempting at a calculation with a large number of mesh points:

(i) calculations involving all three generator coordinates with few (e.g., two) different values for each of them, leading to small matrices (e.g., 8×8 matrices); and

(ii) calculations involving only two generator coordinates the third being held fixed at its variational extremum (e.g., taking a number of values for α_i and β_i, with $\delta=\delta_0$, and so on).

The results of these test calculations have been instructive in that they roughly indicate the effects associated with the different generator coordinates and with their couplings. They are discussed in Sec. V below.

C. Evaluation of the energy and overlap kernels

The procedure followed to obtain the two kernels analytically is completely straightforward (see Ref. 22). As one will immediately recognize upon inspection of Eq. (4.1), the integrations over the internuclear distance R will lead to expressions involving error functions. They were programmed by making use of Hasting's algorithm[24] with an accuracy of better than 7.0×10^{-7}. However, given the value chosen for γ ($\gamma_0=3.2$), the obtained accuracy was in all cases considerably better than this limit. The reduced mass was taken as 908.0764.[21]

D. Numerical procedure

Matrix diagonalizations were performed by the conventional Jacobi method.[25] A test analogous to that utilized in Ref. 12 was used to assess the numerical reliability of the obtained energy eigenvalues, as a check on the absence of ALD problems. All calculations were carried out with double precision on a Digital Equipment Corporation PDP-10 computer.

V. PRELIMINARY TESTS

Small dimensionality runs (typically using two values for each one of three generator coordinates α, β, and δ, leading to 8×8 matrices) were useful to indicate adequate spacings of mesh points. The numbers corresponding to the best calculation of dimension $8=2\times2\times2$ in an extensive series of tests are given in Table I. The mesh points, curiously, do not include the optimal variational values of the generator coordinates [Eq. (4.2)]. In general, the ground-state energy was found to be less sensitive to changes in the values of β than in the values of the other two coordinates; and the values of δ were found to be profitably chosen as rather densely clustered near the optimal variational value δ_0, an expected result in view of the considerable stability of the internuclear separation in H_2^+. In view of the results of Table I, and of the general trend of the results of many small dimensionality runs involving different spacings and positions of mesh points, we choose $\Delta\alpha\approx0.20$, $\Delta\beta\approx0.20$, and $\Delta\delta\approx0.06$ as typical adequate values for setting up the generator-coordinate mesh in larger calculations.

From test runs involving the various combinations of two "active" generator coordinates we have been able to conclude that the most relevant coupling, in the sense that it leads to a substantial lowering of the ground-state energy, occurs between α and δ. Results for a typical calculation involving α and δ as active coordinates are shown in Table II. It may be noted that, as in the case of Table I, the dimensionality of the overlap matrix S corresponds to all the possible combinations of the different values of the two generator coordinates. The Hamiltonian matrix which was diagonalized has a lower dimensionality, however, in view of the adopted truncation parameter ϵ (see Sec. II) which led to discarding three eigenvectors of S. We also found that the inclusion of still more values of α and δ in a calculation such as that shown in Table II was of little help in further reducing the ground-state energy. We, therefore, turned to calculations where all three generator coordinates α, β, and δ were allowed to become active.

TABLE I. "Best" 8×8 calculation. Chosen values for each of the three generator coordinates and resulting energy eigenvalue (for ground state) and dimensions of overlap and energy matrices are given. Energy values are given in atomic units.

α	β	δ	E_0	Matrix dimensions
1.480	0.800	2.020	−0.597 0432	$S=8\times8$
1.680	1.000	2.080		$\tilde{H}=8\times8$

VI. FINAL RESULTS AND DISCUSSION

A. The ground-state energy

In order to obtain further improvement in the ground-state energy without substantially increasing ALD effects or computing time we have added just two additional values of β to the mesh given in Table II, leading to an overlap matrix of dimensionality $75=5\times3\times5$ (see Table III). We kept the truncation parameter fixed at $\epsilon=10^{-12}$, and this produced, in this case, a Hamiltonian matrix of dimensionality 49. The truncation effectively reduces ALD problems for the first few excited states while affecting the lowest eigenvalue in the eighth decimal place only.

The improvement of the ground-state energy, with respect to the calculation shown in Table II, is clear. The footnotes on the excited-state energies given in Table III give the figures affected by ALD problems, as evidenced through the test mentioned in Sec. IV D. As shown, the noise contamination of these results grows progressively as

TABLE II. Calculation involving only α and δ as active generator coordinates. Table arrangement is similar to that of Table I. Also given is the adopted cutoff value for the eigenvalue λ of the overlap matrix, and the order of magnitude of the smallest eigenvalue. Energy values are given in atomic units.

α	β	δ	E_0	E_1	E_2	ϵ	λ_{min}	Matrix dimensions
0.946		1.963	−0.597 1091	−0.587 0473	−0.576 7862	10^{-12}	$\sim10^{-14}$	$S=25\times25$
1.146		2.003						$\tilde{H}=22\times22$
1.346	0.913	2.043						
1.546		2.083						
1.746		2.123						

TABLE III. Calculation involving three active generator coordinates. Table arrangement is similar to that of Tables I and II. "Exact" results for the energy eigenvalues are also quoted from the literature (Ref. 21). Energy values are given in atomic units.

α	β	δ	E_0	E_1	E_2	E_3	ϵ	$\lambda_{\min}$	Matrix dimensions
0.946		1.963	−0.597 1379	−0.587 106[a]	−0.576 861[a]	−0.561 66[b]	10^{-12}	$\sim 10^{-15}$	$S=75\times 75$
1.146	0.713	2.003	−0.597 139 05[c]	−0.587 155 62[c]	−0.577 751 79[c]	−0.568 908 57[c]			$\tilde{H}=49\times 49$
1.346	0.913	2.043							
1.546	1.113	2.083							
1.746		2.123							

[a]Seventh decimal place affected by ALD problems.
[b]Sixth and seventh decimal places affected by ALD problems.
[c]From Ref. 21.

the energy increases. Its level in the present calculation suggests, moreover, that still larger calculations would not be particularly effective in further improving energy values, so that better values should rather be sought by more sophisticated techniques (see Sec. VII below on this point).

In Table IV we also report on a calculation of the same maximum dimensionality as that of Table III, but involving different mesh points. This calculation, in fact, can be seen as done on a mesh which simply adds some extra generator-coordinate values to those given already in Table I. It is remarkable that Tables III and IV give equally good approximations to the exact value of the ground-state energy. This can be qualitatively understood in terms of the following features: (i) the values of δ have in both cases the favored concentration around the variational minimum; (ii) the ground-state energy appears not to be too sensitive to the adopted values for α and β, provided they fall in the ranges $9.00 \lesssim \alpha \lesssim 2.000$ and $0.600 \lesssim \beta \lesssim 1.300$; and (iii) the ground-state energy appears to be rather more sensitive to the *spacings* between mesh points in α and β, ideal choices being $\Delta\alpha \approx 0.20$ and $\Delta\beta \approx 0.20$.

B. The ground-state eigenvector

The most salient feature of the eigenvector associated with the lowest energy eigenvalue is conveniently brought out by expanding it in terms of the eigenvectors $\tilde{\phi}_k$ of the *overlap matrix* [see Eq. (2.3)]:

$$\Psi_0 = \sum_k a_k^{(0)} \tilde{\phi}_k \ . \tag{6.1}$$

In fact, for the calculations reported in Tables III and IV (as well as in all other examined cases, in which the values of δ were concentrated around $\delta \sim 2.000$) it has been found that the expansion (6.1) is strongly dominated by the *single* eigenvector $\tilde{\phi}_0$ of S with largest eigenvalue (typically $a_{k=0}^{(0)} \gtrsim 0.98$). At the same time, of course, the expectation value $\langle \tilde{\phi}_{k=0} | H | \tilde{\phi}_{k=0} \rangle$ is already quite close to the lowest energy eigenvalue as obtained in the calculation. For the first excited eigenvector, a similar result holds for the eigenvector of S with the next-to-highest eigenvalue.

For higher vibrational states this pattern is progressively lost as more and more vectors $\tilde{\phi}_k$ give important contributions to expansions of the type (6.1). The increased relevance of states $\tilde{\phi}_k$ arising from the small norm content of the generator-state base accounts qualitatively for the increase of ALD problems as one goes to higher excitations. On the other hand, the dominance of eigenvectors of S with large eigenvalues in the case of the first few states corroborates "*a posteriori*" the adequacy of the numerical procedure for these states, at least.

In order to check more specifically the degree of similarity of the ground-state eigenvectors given by the calculations of Tables III and IV, respectively (as is well known, the variational energy is not an appropriate criterion for comparison of wave functions), we have also computed two different averages involving the electron-nucleus distance r_a, viz., $\langle r_a^{-1} \rangle$ and $\langle r_a \rangle$ in each of the two wave functions. Results are given in Table V. They show differences in these moments at about the fifth decimal figure. A comparison of the values obtained from the generator-coordinate calculations of Tables III and IV with the best adiabatic and nonadiabatic results given in the literature[26] suggests, moreover, that any of the generator-coordinate wave functions has already incorporated a substantial amount of nonadiabaticity.

TABLE IV. Same as Table III, with a different arrangement of mesh points.

α	β	δ	E_0	E_1	E_2	E_3	ϵ	$\lambda_{\min}$	Matrix dimensions
1.280		1.980	−0.597 1379	−0.587 1187	−0.576 922[a]	−0.565 99[b]	10^{-12}	$\sim 10^{-15}$	$S=75\times 75$
1.480	0.800	2.020							$\tilde{H}=46\times 46$
1.680	1.000	2.060							
1.880	1.200	2.100							
2.080		2.140							

[a]Seventh decimal place affected by ALD problems.
[b]Sixth and seventh decimal places affected by ALD problems.

TABLE V. Values of $\langle r_a^{-1} \rangle$ and $\langle r_a \rangle$ for the ground-state wave functions resulting from the calculations of Table III and IV (in atomic units). Also given are Born-Oppenheimer (BO), adiabatic (AD), and nonadiabatic (NAD) values for the same quantities from the literature.

Parameter	Table III	Table IV	BO Reference 26	AD Reference 26	NAD Reference 26
$\langle r_a^{-1} \rangle$	0.842 51	0.842 50	0.842 82	0.842 69	0.842 49
$\langle r_a \rangle$	1.692 89	1.692 92	1.6925	1.6928	1.6930

VII. FINAL REMARKS AND OUTLOOK

We reported in this paper on a nonadiabatic calculation of the simple H_2^+ molecule using the general framework of the generator-coordinate method as a tool to take maximum advantage of the information already contained in good analytical approximations to the adiabatic wave function. The calculation was performed in an exploratory sense, and we think that the results obtained are encouraging: not only was the value obtained for the ground-state energy extremely accurate, but it was associated to a state having an expansion heavily dominated by a single term in the most natural basis suggested by the formalism. These results were achieved in terms of the diagonalization of matrices of only modest dimensionality (typically of the order 50×50).

We are presently trying to improve on our calculations by introducing still better adiabatic wave functions as generating functions in the place of Eq. (4.1). The use of more sophisticated techniques for setting up the generator-coordinate mesh (see Sec. II) may also be considered. Our basic aim will be to obtain better accuracy for the ground-state energy while keeping within the bounds of a generator-coordinate basis of dimension less than about 75, as done in the present work. More attention will also be paid to the energies and wave functions of excited (vibrational) states.

Other three-body systems such as D_2^+, muonic H_2^+, etc., may also be treated in terms of the present scheme and at essentially the same level of numerical difficulty. Although the procedure is, in principle, quite general, and could be useful whenever good adiabatic functions are available to feed the GC procedure, four-body molecules such as H_2 will already involve a substantially larger computational effort at the present level of technical sophistication. Further investigation of the simpler, three-body systems is therefore in order.

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