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ABSTRACT

We report on a non-adiabatic 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 wavefunctions 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 wavefunctions.

1. 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$^{(3-7)}$. Due 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 using the GCM in a way that allows for non-adiabatic couplings to become operative. We will, in particular, set up the method in such a way as to be able to take maximum advantage of good analytical approximations to the adiabatic wavefunction for the same molecule.

The trial wavefunction 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 wavefunction.

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

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

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

where

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

and

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

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 ressorts to numerical techniques involving a discretized version of this equation. The discretization techniques currently used are reviewed in section 2 below. In section 3 we review some relevant calculations of H_2^+ and then describe an exploratory application of the GCM to this simple system in sections 4 through 6. Section 7 contains some concluding remarks.

2. 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 standard way to satisfy the discretized version of eq. (2.1), i.e.

$$\sum_j (H_{ij} - E_n S_{ij})\, c_j^{(n)} = 0 \qquad (2.2)$$

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 meshpoints 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 as many of the 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 a) on the particular form chosen for the parametrized wavefunction $\phi(\alpha)$ and b) on the particular set of meshpoints 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 $\phi(\alpha)$.

Defering the discussion of point a) to section 4 below, we may note, concerning point b), 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 meshpoints, separated by equal spacings $\Delta\alpha$ or by some other "a priori" prescription, around the single variational optimum α_o which minimizes $E(\alpha) = H(\alpha,\alpha)/S(\alpha,\alpha)$(8).

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

C - Select the $\{\alpha_i\}$ by the interative 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 nonorhtogonality of the basis $\{\phi(\alpha_i)\}$: increasing the number of meshpoints and/or decreasing the separation between meshpoints 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 largest than 10^N, where N is the number of decimal figures carried in the calculations. One particular consequence of the set in of ALD is that the upper bound variational property of the energy will be progressively obfuscated by numerical inaccuracies.

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 GC calculation which can be sumarized 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

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

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

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

which makes the source of trouble apparent through the occurence of terms in the sum with vanishingly small denominators (the small eigenvalues of the overlap matrix). Thus

(iii) Truncate Hamiltonian matrix (2.4) by eliminating all eigenvectors $\tilde{\Phi}_k$ associated with eigenvalues λ_k of S_{ij} smaller than a suitable limit ϵ. 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 $\tilde{H}_{k\ell}$ with the lowest eigenvalues, while still being able to generate unwanted numerical noise if carried in the calculation.

3. H_2^+ CALCULATIONS: A SURVEY

A. Discretized GC adiabatic calculations. We mention here three electronic variational GC calculation for H_+^2 which however make no explicit reference to the GCM$^{(11,14,15)}$. The first of these (ref. (11)) makes use of the procedure D (see section 2) 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. Non-adiabatic calculations.

B.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)

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

where ϵ , η are two electronic coordinate in concofocal elliptical coordinates and R is the internuclear distance. These functions involve four non-linear variational parameters α, β, γ and δ, $H_n(R-\delta)$ are Hermite polinomials. The value of the ground state energy obtained in ref. (17) with an expression involving 57 terms is -0.5971387 a.u. (the best adiabatic value being -0.5971385 a.u., see ref. (18)). An expansion involving 176 terms yielded the value -0.59713905 a.u. (ref. (18)) and, when pushed to nearly 500 terms, the value -0.59713906 a.u. (ref. (19)).

B.2. Perturbation calculations. The non-adiabatic variational calculations described above have not, until now, taken full advantage of the information contained in exact adiabatic wavefunctions, 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 the values of ref. (18)(optimized for the entire expansion) the resulting ground state energy is very poor. In 1967 Hunter and Pritchard were able to obtain the value -05971387 a.u. adopting a perturbation treatment starting from the adiabatic ground state wavefunction and mixing in two adiabatic excited states. Further improvement along these lines was however hard to obtain. In 1978 Wolniewics and Pohl (21) were able to obtain the value -059713905 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 non adiabatic calculation appears to be available to date for H_2^+ .

4. NON-ADIABATIC GC CALCULATION FOR H_2^+

Why should one attempt at another non-adiabatic 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 wavefunctions 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 wavefunction for the lowest eigenstate (a J=0 , v=0 state), $\phi_0^{Ad} = \varphi_0^{e\ell} \chi^{nuc}$. One is freed from the requirement of including excited electronic states in order to allow for nonadiabaticity since non-diagonal matrix elements $H(\alpha,\alpha')$ involving wavefunctions 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 $\{\phi_0^{Ad}(\alpha_i)\}$ 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 holds of course also for the overlap matrix $S(\alpha_i,\alpha_j)$.

4.1. CHOOSING THE GENERATING FUNCTION $\phi(\alpha)$

We restrict ourselves in this work to rotationaly 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 generating function the adiabatic wavefunction$^{(22)}$

$$\phi(\alpha,\beta,\delta) = \varphi_{GZ}(r_A,r_B;\alpha,\beta)\ X(R,\delta) =$$

$$= \exp\left[-\alpha(r_A+r_B)\right]\left[\exp(-\beta r_A)+\exp(-\beta r_B)\right]$$

$$\times \exp\left[-\frac{\gamma^2}{2}(R-\delta)^2\right] \quad . \tag{4.1}$$

The electronic factor φ_{GZ} is the Gillemin-Zener wavefunction$^{(23)}$. Optimal variational values for α, β, γ and δ, determined by Diehl and Flügge$^{(22)}$, are

$$\alpha_o = 1.346 \ ; \ \beta_o = 0.913 \ ; \ \gamma_o = 3.200 \ ; \ \delta_o = 2.043 \tag{4.2}$$

leading to the value -0596430 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_o. 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 meshpoints. The choice of these is discussed in the next subsection. 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 essentialy with nuclear vibrational excitations.

4.2. CHOOSING THE GC MESHPOINTS

We have adopted the procedure A (see section 2), in its simplest form, for selecting the GC meshpoints: a fixed interval was chosen for each one of the three generator coordinates, and a variable number of points was used in the neighborhood of the variationally optimal values given in (4.2). Moreover, it has been found useful to carry out two types of preliminary probing tests before attempting at a calculation with a large number of meshpoints:

(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).

(ii) calculations involving only two generator coordinates, the third being held fixed at its variational extremum (e.g. taking a number of values α_i , β_i with $\delta=\delta_o$ 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 section 5 below.

4.3. EVALUATION OF THE ENERGY AND OVERLAP KERNELS

The procedure followed to obtain the two kernels analytically is completely straighforward (see ref. (22)). As on 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 programed by making use of Hasting's algorithm$^{(24)}$ with an accuracy better than 7.0×10^{-7}. However, given the value chosen for γ ($\gamma_o=3.2$) the obtained accuracy was in all cases considerably better than this limit. The reduced mass was taken as 908.0764$^{(21)}$.

4.4. 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 PDP-10 computer.

5. 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 meshpoints. The numbers corresponding to the best calculation of dimension $8=2\times2\times2$ in an extensive series of tests are given in Table 1. The meshpoints 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_o , an expected result in view of the considerable stability of the internuclear separation in H_2^+ . In view of the results of Table 1, and of the general trend of the results of many small dimensionality runs involving different spacings and positions of meshpoints, 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 2. It may be noted that, as in the case of Table 1, 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 section 2) which led to discard 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 2 was of little help to further reduce the ground state energy. We therefore turned to calculations where all three generator coordinates α, β and δ were allowed to become active.

6. FINAL RESULTS AND DISCUSSION

6.1. 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 2 above, leading to an overlap matrix of dimensionality $75 = 5\times3\times5$ (see Table 3). 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 ALC 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 2, is clear. The dots in the last decimal places of the excited state energies given in Table 3 correspond to the figures affected by ALD problems, as evidenced through the test mentioned in section 4.4. As shown, the noise contamination of these results grows progressively as 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 section 7 below on this point).

In Table 4 we also report on a calculation of the same maximum dimensionality as that of Table 3, but involving different meshpoints. 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 1. It is remarkable that Tables 3 and 4 give equally good approximation 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 $0.600 \lesssim \beta \lesssim 1.300$; (iii) the ground state energy appears to be rather more sensitive to the <u>spacings</u> between meshpoints in α and β, ideal choices being $\Delta\alpha \approx 0.20$ and $\Delta\beta \simeq 0.20$.

6.2. THE GROUND STATE EIGENVECTOR

The most salient feature of the eigenvector associeated with the lowest energy eigenvalue is conveniently brought out by expanding it in terms of the eigenvectors $\tilde{\phi}_k$ of the <u>overlap matrix</u> (see eq. (2.3)):

$$\Psi_o = \sum_k a_k^{(o)} \tilde{\phi}_k \tag{6.1}$$

In fact, for the calculations reported in Tables 3 and 4 (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 <u>single</u> eigenvector

$\tilde{\phi}_o$ of S with largest eigenvalue (typically $a^{(o)}_{k=0} \geq 0.98$). 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 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 3 and 4 respectively (as is well known, the variational energy is not an appropriate criterion for comparison of wavefunctions) 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 wavefunctions. Results are given in Table 5. 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 3 and 4 with the best adiabatic and non-adiabaric results given in the literature$^{(27)}$ suggests moreover that any of the generator-coordinate wavefunctions has already incorporated a substantial amount of non-adiabaticity.

7. FINAL REMARKS AND OUTLOOK

We reported in this paper on a non-adiabatic 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 wavefunction. 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 wavefunctions as generating functions in the place of eq. (4.1). The use of more sophisticated techniques for setting up the Generator Coordinate mesh (see section 2) 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 wavefunctions of excited (vibrational) states.

TABLE CAPTIONS

TABLE 1 - The "best" 8×8 calculation. Chosen values for each of the three generator coordinates are given on top. Resulting energy eigenvalue (for ground state) and dimensions of overlap and energy matrices are given below. Energy values are given in atomic units.

TABLE 2 - Calculation involving only α and δ as "active" generator coordinates. Table arrangement is similar to that of Table 1. Also given is the adopted cut-off 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.

TABLE 3 - Calculation involving three "active" generator coordinates. Table arrangement is similar to that of Tables 1 and 2. "Exact" results for the energy eigenvalues are also quoted from the literature (ref. (21)). Energy values are given in atomic units.

TABLE 4 - Same as Table 3, with a different arrangement of meshpoints.

TABLE 5 - Values of $<r_a^{-1}>$ and $<r_a>$ for the ground state wavefunctions resulting from the calculations of Tables 3 and 4 (in atomic units). Also given Born-Oppenheimer (BO), Adiabatic (AD) and Non-adiabatic (NAD) values for the same quantities from the literature.

TABLE 1

α	1.480	1.680
β	0.800	1.000
δ	2.020	2.080
E_o	- 0.5970432	
		Matrix dimensions S: 8×8 $\tilde{H}$: 8×8

TABLE 2

α	0.946	1.146	1.346	1.546	1.746
β			0.913		
δ	1.963	2.003	2.043	2.083	2.123
E_o	$-$ 0.5971091				
E_1	$-$ 0.5870473				
E_2	$-$ 0.5767862				
$\epsilon = 10^{-12}$ $\lambda_{min} \sim 10^{-14}$	Matrix dimensions $S = 25\times25$ $\tilde{H} = 22\times22$				

TABLE 3

α	0.946	1.146	1.346	1.546	1.746
β		0.713	0.913	1.113	
δ	1.963	2.003	2.043	2.083	2.123
E_o	$-$ 0.5971379	(present work)	$-$ 0.59713905	ref.(21)	
E_1	$-$ 0.587106.	(present work)	$-$ 0.58715562	ref.(21)	
E_2	$-$ 0.576861.	(present work)	$-$ 0.57775179	ref.(21)	
E_3	$-$ 0.56166..	(present work)	$-$ 0.56890857	ref.(21)	
ϵ λ_{min}	10^{-12} $\sim10^{-15}$	Matrix dimensions $S = 75\times75$ $\tilde{H} = 49\times49$			

TABLE 4

α	1.280	1.480	1.680	1.880	2.080
β		0.800	1.000	1.200	
δ	1.980	2.020	2.060	2.100	2.140
E_o	− 0.5971379				
E_1	− 0.5871187				
E_2	− 0.576922.				
E_3	− 0.56599..				
ϵ	10^{-12}		Matrix dimensions S: 75×75 $\tilde{H}$: 46×46		
λ_{min}	$\sim 10^{-15}$				

TABLE 5

	Table 3	Table 4	Bo$^{(ref.27)}$	AD$^{(ref.27)}$	NAD$^{(ref.27)}$
$\langle r_a^{-1} \rangle$	0.84251	0.84250	0.84282	0.84269	0.84249
$\langle r_a \rangle$	1.69289	1.69292	1.6925	1.6928	1.6930

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