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Molecular Schrödinger–Riccati calculations: The potential energy curve of the hydrogen molecule

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The Schrödinger–Riccati equation has been used in the study of the potential energy curve of the Hydrogen molecule. The minimum is obtained at the equilibrium bond distance. The predicted total energy at that point is -1.1727 hartree, with a relative error (in absolute value) of 0.15% with respect to the exact energy of -1.1745 hartree.

KEY WORDS: Schrödinger–Riccati equation, hydrogen molecule, local energy

1. Introduction

The Schrödinger–Riccati equation (SRE) [1,2] represents an alternate approach for the local study of the Schrödinger equation within the framework of the local energy methods (LEM). The designation Schrödinger–Riccati reflects the fact that it was obtained through the use of a Riccati equation. It has been tested for the one-dimensional Schrödinger equation [2], H and Be atoms [3,4] and the Hydrogen-ion molecule [5]. (A comprehensive review of LEM has been given in a previous work [2].)

The numerical application of the SR-formulation requires the availability of a starting function and an estimate of the energy of the system. This estimate is changed in successive calculations, until concordance (to the desired precision) with the predicted energy is obtained.

The calculations are performed for a chosen sampling region and yield a statistical result. The quality of the calculation is judged by the concordance

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between the input energy and the sample mean energy as well as by the standard deviation of the latter. A comparison with the corresponding results for the starting function will confirm the improvement obtained.

The hydrogen molecule is a favourite testing ground for new theoretical methods and it is well known the accurate potential energy curve of the ground state [6]. In this work the SRE has been used for the study of the potential energy curve of the H_2 molecule in the vicinity of the equilibrium bond distance.

2. Theoretical background

Given the Schrödinger equation

$$(\mathcal{H} - E)\Psi \equiv (T + V - E)\Psi = 0 \tag{1}$$

where $\mathcal{H}$ is the Hamiltonian operator (consisting of the kinetic and potential energy operators, T and V, respectively) and Ψ and E denote one of its eigenfunctions and corresponding eigenvalue, the associated local SRE [1,2] is

$$(V - E)\Psi + \sum_{n=0}^{\infty} \frac{1}{n!} T^{(n)} \varphi^n = 0 \tag{2}$$

where the function φ represents the correction that must be added to an approximate function Φ in order to generate an improved approximation to the correct eigenfunction, $\Psi = \Phi + \varphi$.

The quantities $T^{(n)}$ are defined by

$$T^{(n)} = \frac{\partial^n (T\Phi)}{\partial \Phi^n} \tag{3}$$

and their expressions are obtained by the chain rule, with auxiliary differentiation with respect to one of the parameters (usually the exponent of one of the basis functions) in Φ.

As starting function one can use any of the spatial components (consisting of a single monomial term or of a linear combination of monomial terms), with a given associated spin component, of an approximate function.

2.1. Evaluation of the correction function

The practical application of the SR-equation implies solving equation (2), with a given input value of the energy (E_i), at points in the electron configuration space (ECS) in order to determine the corresponding local values of the correction function φ. In these calculations equation (2) is truncated at a finite value of n (usually $n = 4$), with subsequent improvement of the solution by a direct search procedure.

2.2. Evaluation of the local energy

The calculation for the prediction of the energy involves the evaluation of the correction function and of its energy contribution. The values of the second derivatives of φ with respect to x, y, and z are needed in the second step. The corresponding expressions may be obtained by differentiation of equation (2):

$$\partial\varphi = -\frac{1}{D}\{\Psi\partial V + (V - E)\partial\Phi + A_1\} \tag{4}$$

$$\partial^2\varphi = -\frac{1}{D}\{\Psi\partial^2 V + 2\partial\Phi\partial V + (V - E)\partial^2\Phi + A_2 + 2(\partial V + C_1)\partial\varphi + B_2(\partial\varphi)^2\} \tag{5}$$

where ∂ and ∂^2 stand for the first and second derivatives with respect to x, y, or z and

$$A_1 = \sum_{n=0} \frac{1}{n!}\partial T^{(n)}\varphi^n \tag{6}$$

$$A_2 = \sum_{n=0} \frac{1}{n!}\partial^2 T^{(n)}\varphi^n \tag{7}$$

$$B_1 = \sum_{n=1} \frac{1}{(n-1)!} T^{(n)}\varphi^{n-1} \tag{8}$$

$$B_2 = \sum_{n=2} \frac{1}{(n-2)!} T^{(n)}\varphi^{n-2} \tag{9}$$

$$C_1 = \sum_{n=1} \frac{1}{(n-1)!}\partial T^{(n)}\varphi^{n-1} \tag{10}$$

$$D = (V - E) + B_1 \tag{11}$$

The energy obtained in such a procedure will represent, as a rule, an approximate local energy, being different from the value used as input energy. In this work the local energies are evaluated with a precision of five significant figures.

2.3. Evaluation of a mean value of the energy

An extended calculation for a chosen sampling region will allow us to obtain a statistical estimate of the mean energy of the system under consideration.

The result will depend on the sampling region and, therefore, a search for an appropriate region must be carried out. The chosen region should be characterized by a *quasi*-constancy of the local energy values, as evidenced by a small standard deviation. In addition, the input energy should lie within (or close to) the confidence interval [7] of the sample mean energy. The starting function, as a rule, will not show that *quasi*-constancy or it will not show it in a region of appreciable size.

The distances, angles, and energies are given in bohr, degree, and hartree, respectively, throughout the text.

3. Application to the groundstate of the hydrogen molecule

The starting function used is

$$\Phi = \phi(1)\phi(2)$$

where ϕ represents a linear combination (LCAO) of $1s$ basis functions centred on each nucleus. The associated spin function is $\alpha(1)\beta(2)$, where α and β denote the usual spin functions. Identical values are used for the exponents of the two basis functions. The value 1.18 is used for the equilibrium bond distance. That value is decreased progressively as the bond distance is increased and will approach the value 1.0 at large separations of the nuclei.

All the local values of the starting function were mutiplied by the same constant, in order to avoid very small values. The local values of the correction and the resulting functions are obtained multiplied by that same factor but the predicted local energies are not affected.

The Cartesian system of coordinates is centred at the midpoint of the bond (see figure 1), which lies on the z-axis. The positions of the electrons will be specified by their polar spherical coordinates (the distance r to the centre of coordinates and the azimuth and colatitude angles). Taking into account symmetry considerations, the azimuth angles of both electrons are kept constant (at a value 0°). The colatitude angle (θ) of the first electron will be varied from 90° (when the electron lies on the line perpendicular to the bond at its midpoint) through 0° (when the electron lies on the molecular axis). The colatitude angle of the second electron will be decreased from an initial value of 180°; its final value will be chosen on the basis of the standard deviation obtained in the statistical calculation.

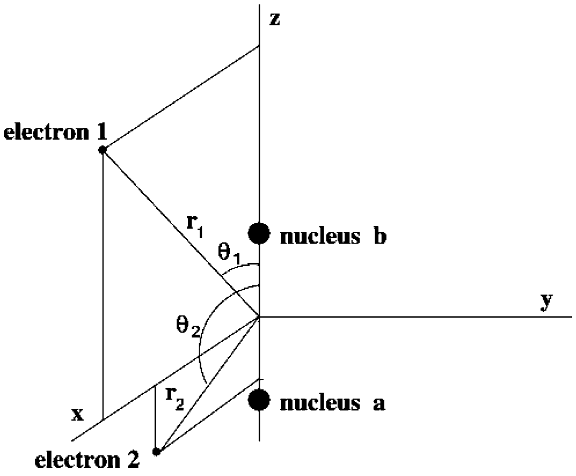

Figure 1. Cartesian system of coordinates for the Hydrogen molecule.

Preliminary calculations were carried out in order to locate a region in the ECS in which the absolute values of the starting function will be small, with the expectation that the absolute value of the correction function, and consequently of the possible error, will also be small. The initial electron configuration is defined by the following polar coordinates (r, azimuth, colatitude): electron 1 – 3.0 bohr, 0°, 90°; electron 2 – 2.5 bohr, 0°, 180° (see figure 1). The sampling region will be generated by varying r and the colatitude angle of electron 1 (with respective increments of 0.1 bohr and 1.0°) and the colatitude angle of electron 2 (with an increment of $-1.0°$). [Herefater the increments will only be given explicitly if they are different from the above values.] The sampling regions will be labelled as $nr_1/nc_1/nc_2$, where nr_1, nc_1, and nc_2 denote the number of points in the r_1-interval and in the intervals for the variation of the colatitude angles of the two electrons, respectively.

In a predictive calculation it is necessary, first of all, to determine the interval in which the exact energy will be found. In the present case calculations were performed for the regions 21/19/1 (with increment of 5°) and 21/91/1 (with increment of 1°), with input electronic energies around -1.89 hartree. The possible total number of points were 399 and 1911. The results, presented in table 1, indicate that concordance between the input and the predicted sample mean energies will occur for a value close to -1.890 hartree.

When using the accurate energy, -1.888761 hartree [6], the sample mean energies have standard deviations of 0.01685 and 0.01741, respectively. The quality of these results is confirmed by the behaviour of the predicted function. Figure 2 presents the plots of the ratios $\Phi_{\mathrm{LCAO}}/\Psi_{\mathrm{FB}}$ and $\Psi_{\mathrm{SR}}/\Psi_{\mathrm{FB}}$, where Ψ_{SR} is the function predicted in this work and Ψ_{FB} denotes a correlated function, first proposed by Frost and Braunstein [8], of the type $\Phi(1.0 + 0.28\ r_{12})$, where

Table 1
Search of appropriate input energy: Predicted energies for different input energies[a]

	Region	
Input energy	21/19/1	21/91/1
−1.880	−1.8840	−1.8846
−1.888761	−1.8882	−1.8888
−1.890	−1.8889	−1.8894
−1.900	−1.8934	−1.8942

[a] At the equilibrium bond distance. The energies are given in hartree. See the text for details of the sampling.

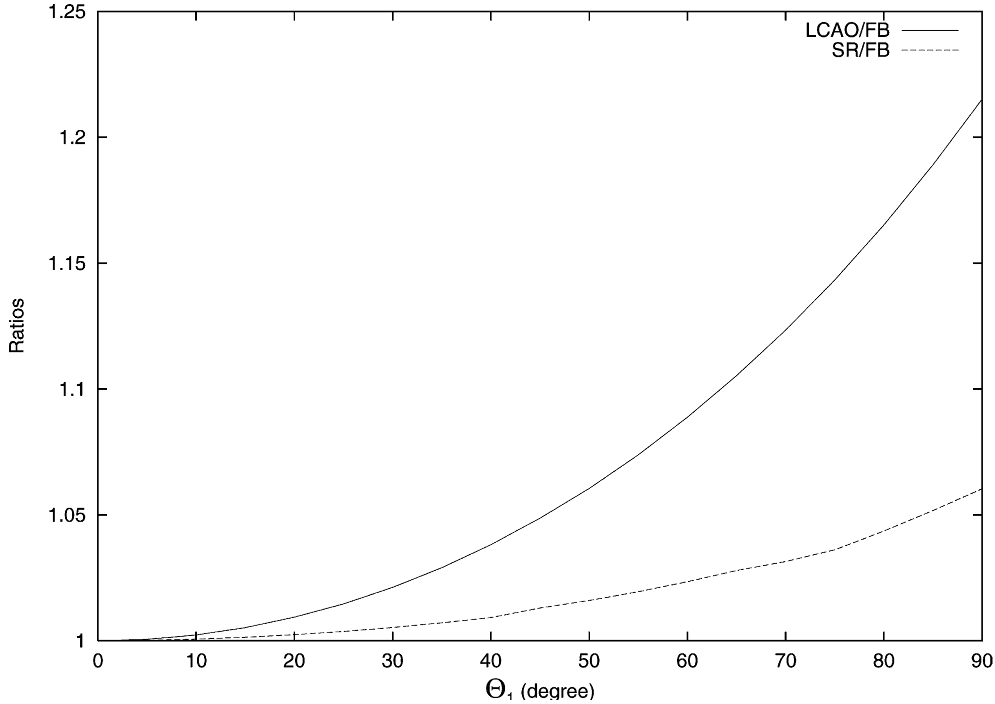

Figure 2. Plots of the ratios $\Phi_{\rm LCAO}/\Psi_{\rm FB}$ and $\Psi_{\rm SR}/\Psi_{\rm FB}$. The coordinate values in each curve have been divided by the coordinate of the first point in the curve. The abscissas are the values of the colatitude angle of the first electron.

r_{12} denotes the interelectronic separation. The results were obtained for a region 1/19/1, with $r_1 = 4.0$ bohr and the colatitude angle of the first electron varied from 0 to 90°. When examining this figure it must be realized that the correlated function used for the comparison is not the exact function. The difference in the behaviour observed for the starting function and for the SR-function clearly indicates that the SR-formalism has incorporated a correlation correction, which is missing in the starting function.

Taking the above results into account, the accurate energies will be used hereafter as input. The calculations will be carried out for various bond distances, around the equilibrium position, for the sampling region 21/91/25, for a possible total number of 47,775 points. [For greater bond distances it would be necessary to change the first interval.] At most points, calculations have been performed for several orbital exponents and the selection of the appropriate result has been done on the basis of a closer concordance with the input energy. The results, presented in table 2, confirm that the SR-formalism may be used for the prediction of potential energy curves. It must be pointed out, however, that for a more precise prediction it would be necessary to carry out more extensive calculations. For each internuclear separation the calculations should be performed for a series of input energies, with different orbital exponents. The difference between the predicted and the input energy at each separation must be smaller than the differences between the predicted energy at that separation and the predicted energies for the two adjacent points in the curve.

In this connection two comments are pertinent regarding the size of the sampling region and the number of points given in table 2. Those are the points at which the calculation was successful. The calculations failed at a small number (less than 2% of the possible total number) of points because a fixed number of terms was used in the expansions. An appropriate increase in the number of terms in the expansions would ensure that the calculation would succeed at all

Table 2
Partial prediction of the potential energy curve [a]

Bond distance	Orbital exponent	Total energy		No. of points	Standard deviation (SD)
		Predicted	Accurate [6]		
1.0	1.24	−1.1238	−1.1245	46,863	0.02142
1.2	1.21	−1.1651	−1.1649	47,240	0.01691
1.3	1.20	−1.1705	−1.1723	47,250	0.02153
1.4	1.18	−1.1727	−1.1745	46.862	0.01677
1.5	1.17	−1.1725	−1.1729	47,267	0.01481
1.6	1.16	−1.1693	−1.1686	47,021	0.01465
1.8	1.13	−1.1566	−1.1551	47,010	0.02020

[a] For the sampling region 21/91/25, using the accurate electronic energies [6] as input. The bond distances are given in bohr and the energies in hartree. See the text for details of the sampling region.

Table 3
Dissociation limit[a]

		LCAO		SR	
No. of points	r-increment	Energy	SD	Energy	SD
11	0.5	−0.9933	0.00222	−1.0034	0.00749
21	0.25	−0.9933	0.00212	−1.0024	0.00556
41	0.125	−0.9932	0.00206	−1.0018	0.00410
51	0.1	−0.9932	0.00205	−1.0016	0.00371
101	0.05	−0.9932	0.00203	−1.0014	0.00274
201	0.025	−0.9932	0.00202	−1.0013	0.00216

[a] For a sampling region $nr_1/1/1$ with the colatitude angles of the electrons set at 0 and 180°, respectively, at a bond distance of 10.0 bohr. The total energies are given in hartree.

the points. It was considered that there was no need to undertake such a step because of the large effective size of the sampling region, as shown by the following argument. The azimuth angles of the two electrons were maintained fixed, at a value 0°, for the calculations reported in table 2. The same results would have been obtained, however, for all those sampling regions, identical to the one above but with (equal) azimuth angles of the two electrons ranging from 0 to 360°. That is, the total energies given in table 2 correspond to a sampling region covering a considerable part of the ECS.

A final calculation was next performed for a bond distance of 10.0 bohrs in order to show that the SR-formalism will lead to the correct dissociation limit. The electron configuration (r, azimuth angle, colatitude angle) used was: electron 1 (6.0, 0, 0); electron 2 (7.0, 0, 180). The r_1-interval extended from 6.0 through 11.0 bohr and the angles of the two electrons were kept fixed. The orbital exponents of the two basis functions were set to 1.00. The corresponding results are presented in table 3. The predicted total energy, −1.0012 hartree, has an error (in absolute value) of 0.12% with respect to the exact value [6] of −1.0001 hartree.

An interesting point to be observed in table 3 is the convergence behaviour with increasing number of points in the sampling region. This behaviour further supports the discussion given above regarding the number of successful points: the mean sample energy has essentially converged already (to an accuracy of five significant figures) with only 201 points.

4. Conclusions

It has been intended, with this work, to show that the SR-formalism is appropriate for the study of molecular systems and capable of accounting for the correlation correction.

The calculations have yielded, at the level of precision adopted, a satisfactory prediction of the potential energy curve of the Hydrogen molecule, regarding the position of the minimum and the dissociation limit.

At the equilibrium internuclear separation, the predicted total energy, −1.1727 hartree, has a relative error (in absolute value) of 0.15% with respect to the accurate energy, −1.1745 hartree. A comparable error, 0.12%, is obtained at a nuclear separation of 10.0 bohr, confirming that a satisfactory prediction of the dissociation energy may be made.

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