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# Molecular Schrödinger–Riccati calculations. Test for the hydrogen-ion molecule

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**Abstract.** The hydrogen-ion molecule has been used as a test system for the application of the Schrödinger–Riccati formulation to molecular calculations. Some of the points discussed are the characteristics (quasiconstancy of the local energies, size, number of points) of the sampling region to be chosen, the dependence on the starting function, the precision of the calculations, and the excellent behaviour of the predicted function (by comparison to an accurate function).

**Key words:** Schrödinger–Riccati equation – Hydrogen-ion molecule – Local energy

## 1 Introduction

The Schrödinger–Riccati equation (SRE) represents [1] a new approach within the framework of the local energy method, reviewed in recent work [2], where details and references may be found. The designation Schrödinger–Riccati (SR) was adopted because the equation was derived through the use of a Riccati equation. This equation has been tested in the study of the one-dimensional Schrödinger equation [2] and the ground state of the hydrogen atom [3].

The SRE may be used, starting from an approximate function, for the evaluation of improved local values of both the function and the energy of any bound state of the system under consideration. The improvement of the function will not be the same at every point in the electron configuration space (ECS) and, consequently, the local values of the energy will vary. The constancy of the local values of the energy will only be reached when the improvement yields the exact value of the function at each point.

In order to overcome this difficulty, when aiming at a prediction of an estimate of the energy of the system, it is necessary to make recourse to the evaluation of a mean value for a given sampling region. Such a procedure may be considered to constitute an approximation to the averaging carried out in a traditional quantum-mechanical calculation when evaluating the energy expectation value.

The hydrogen-ion molecule was chosen, because of the availability of the exact energy values for a number of bond lengths [4], in order to determine whether the sampling procedure may yield a satisfactory estimate of the electronic energy. The quality of the predicted function will be judged by comparison with the accurate function of Weinhold and Chinen [5]. (This accurate function was chosen for its simplicity. References to other studies of this system may be found in that work.)

## 2 Theoretical background

Given the Schrödinger equation

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

where $\mathscr{H}$ is the Hamiltonian operator (consisting of the kinetic energy and potential-energy operators, $T$ and $V$, respectively) and $\Psi$ and $E$ denote one of its eigenfunctions and the 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 $\varphi$ represents the correction that must be added to an approximate function $\Phi$ in order to generate an improved approximation to the correct eigenfunction, $\Psi = \Phi + \varphi$. The quantities $T^{(n)}$ are defined by

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

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 $\Phi$.

The details of the derivation of the SRE may be found in previous work [1, 2] and here we just summarize the actual procedure for numerical calculations.

### 2.1 *Determination of the correction function*

The practical application of the SRE implies solving Eq. (2), with a given input value of the energy $(E_i)$, at points in the ECS, in order to determine the corresponding local values of the correction function $\varphi$. The quantities $T^{(n)}$ are obtained from the chosen starting function, which can be any of the spatial components (consisting of a single monomial term or of a linear combination of monomial terms), associated with a given spin component, of an approximate function.

In the calculations, the approximate value of $\varphi$, obtained from Eq. (2) truncated at $n = 4$, is then improved through an iterative search procedure. Then, the energy contribution of $\varphi$ is evaluated and the local energy of the system is obtained.

### 2.2 *Evaluation of the local energy*

In the present case, the value of the local energy at the point under consideration is given by

$$E = V - \frac{1}{2} \frac{\left[\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)(\Phi + \varphi)\right]}{(\Phi + \varphi)} \quad . \tag{4}$$

The derivatives of $\varphi$, which are obtained by differentiation of Eq. (2), are given by

$$\partial\varphi = -\frac{1}{D}[\Psi \partial V + (V - E)\partial\Phi + A_1] \ , \tag{5}$$

$$\partial^2\varphi = -\frac{1}{D}\Big[\Psi\partial^2 V + 2\partial\Phi\partial V + (V - E)\partial^2\Phi + A_2. \\ + 2(\partial V + B_1) + B_2(\partial\varphi)^2\Big] \ , \tag{6}$$

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

$$A_1 = \sum_{n=0} \frac{1}{n!} \partial T^{(n)} \varphi^n \ , \tag{7}$$

$$A_2 = \sum_{n=0} \frac{1}{n!} \partial^2 T^{(n)} \varphi^n \ , \tag{8}$$

$$B_1 = \sum_{n=1} \frac{1}{(n-1)!} T^{(n)} \varphi^{n-1} \ , \tag{9}$$

$$B_2 = \sum_{n=2} \frac{1}{(n-2)!} T^{(n)} \varphi^{n-2} \ , \tag{10}$$

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

The energy obtained in such a procedure will represent, as a rule, an approximate local energy, being different from the value used as the input energy. In this work these local energies are evaluated to 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 the most appropriate region must be carried out. The region to be chosen, when using a given input energy, will be the one for which acceptable values are obtained for both the confidence interval for the calculated mean energy and the error of the latter with respect to the input energy.

All the energies are given in hartree throughout the text.

## 3 Numerical results

The starting function used for the ground state of the hydrogen-ion molecule is $\Phi = \phi(1)$, where $\phi$ is the molecular orbital built up as a linear combination of 1*s* atomic orbitals (LCAO) centred on each atom. The initial value of the orbital exponent of each atomic orbital was set to 1.0.

All the local values of the starting function were multiplied by the same constant in order to avoid very small values. The local values of the correction and the resulting functions obtained were multiplied by that

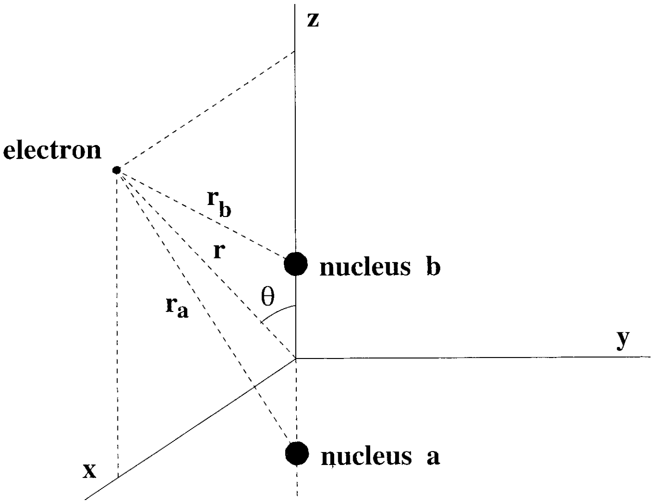

**Fig. 1.** Cartesian system of coordinates for the hydrogen-ion molecule

same factor but the predicted local energies were not affected.

The Cartesian system of coordinates is centred at the midpoint of the bond (Fig. 1), which lies on the $z$-axis. The position of the electron will be specified by its confocal elliptic coordinates: $\lambda = (r_a + r_b)/R$ and $\mu = (r_a - r_b)/R$, where $r_a$ and $r_b$ denote the distances of the electron from each nucleus and $R$ is the bond length. In some instances, however, the position of the electron will be identified by its polar coordinates, $r$ and $\theta$; taking into account symmetry considerations, the value of the latter will be restricted to the interval from 0° (when the electron lies on the molecular axis) to 90° (when the electron lies on the line perpendicular to the bond at its midpoint). (The other polar angle is always kept constant at a value of 0°.)

Preliminary calculations were carried out in order to locate a region in the ECS in which the absolute values of the starting function are small, with the expectation that the absolute value of the correction function, and consequently of the possible error, will also be small. A simple calculation, not requiring the solution of the SRE, suggested that the interval $10.0 \leq r \leq 20.0$ bohr would be appropriate.

Calculations were then performed for three sampling regions, with that $r$ interval and $\theta = 0, 45$, and 90°, respectively. With $\Delta r = 1.0$ bohr, each calculation yielded 11 local energies, which were used for the evaluation of the corresponding sample mean energy and its standard deviation. The results presented in Table 1, which show a quasiconstancy of the SR local electronic energies, were obtained at the equilibrium bond length, with the exact energy as an input. The values for the starting LCAO function are also presented in Table 1 in order to show the difference in the behaviour of the LCAO and SR energies. The quasiconstancy of the local SR energies suggests that the $r$ interval is appropriate; this observation is confirmed by similar results obtained for the three sample mean energies. The quasiconstancy of the local SR energies, together with the size of the region, are the decisive factors in the selection of the appropriate sampling region. It might be possible to find a small sampling region in which even the local energies of the starting function would show a quasiconstancy, but it will still be possible to observe the improvement introduced by the SR formulation. In the present case that improvement is evident from the values for the standard deviations of both the LCAO and the SR values.

Several extended sampling regions, related to the ones described earlier but with consideration of the complete $\theta$ interval (from 0 to 90°), were considered next. The calculations were again performed for the equilibrium bond length and with the same input energy as earlier. As seen in Table 2, the region covering the interval $10 \leq r \leq 23$ bohr seems to be the most appropriate, as it leads to the sample mean closest to the input energy; this conclusion is confirmed by results presented in Tables 3, 4, 5, 6, and 7. (In a predictive calculation,

**Table 2.** Results for various sampling regions. The values of $r$ are in bohr. The angle $\theta$ is varied from 0 to 90°, with a constant increment of 1°

| $r$ interval | Number of points | Electronic energy | |
|---|---|---|---|
| | | Mean value | Standard deviation |
| 6–24 | 16,470 | −1.09631 | 0.01641 |
| 8–24 | 14,650 | −1.10155 | 0.00402 |
| 10–24 | 12,831 | −1.10241 | 0.00085 |
| 10–23 | 11,921 | −1.10261 | 0.00036 |
| 10–22 | 11,011 | −1.10269 | 0.00019 |
| 10–20 | 9,191 | −1.10276 | 0.00013 |
| 10–18 | 7,371 | −1.10279 | 0.00012 |
| 10–16 | 5,551 | −1.10283 | 0.00012 |

**Table 3.** Local values of the ratio of the predicted function over an accurate function. The electron is found at a distance of 6.0 bohr from the internuclear axis in all cases. The predicted function was multiplied by a constant such that it yields a value of 1 for the first entry. See Ref. [5] for details of the accurate function

| $\lambda$ | $\mu$ | Ratio | $\lambda$ | $\mu$ | Ratio |
|---|---|---|---|---|---|
| 6.08 | 0.00 | 1.000 | 6.68 | 0.42 | 0.924 |
| 6.11 | 0.09 | 0.999 | 6.98 | 0.50 | 0.899 |
| 6.17 | 0.17 | 0.986 | 7.37 | 0.57 | 0.877 |
| 6.29 | 0.26 | 0.970 | 7.87 | 0.64 | 0.869 |
| 6.45 | 0.34 | 0.950 | 8.52 | 0.71 | 0.882 |

**Table 1.** Predicted local electronic energies at the points of three sampling regions. The distance, $r$, of the electron from the centre of coordinates is given in bohr and the angle $\theta$ in degree. See the text for details

| $r$ | $\theta = 0$ | | $\theta = 45$ | | $\theta = 90$ | |
|---|---|---|---|---|---|---|
| | LCAO | SR | LCAO | SR | LCAO | SR |
| 10 | −0.59332 | −1.10315 | −0.59596 | −1.10312 | −0.59950 | −1.10310 |
| 11 | −0.58532 | −1.10297 | −0.58755 | −1.10296 | −0.59054 | −1.10294 |
| 12 | −0.57859 | −1.10286 | −0.58050 | −1.10285 | −0.58305 | −1.10284 |
| 13 | −0.57285 | −1.10279 | −0.57449 | −1.10279 | −0.57670 | −1.10278 |
| 14 | −0.56789 | −1.10275 | −0.56933 | −1.10274 | −0.57125 | −1.10274 |
| 15 | −0.56356 | −1.10272 | −0.56483 | −1.10271 | −0.56652 | −1.10271 |
| 16 | −0.55976 | −1.10270 | −0.56088 | −1.10269 | −0.56238 | −1.10269 |
| 17 | −0.55638 | −1.10268 | −0.55739 | −1.10267 | −0.55872 | −1.10268 |
| 18 | −0.55337 | −1.10266 | −0.55427 | −1.10266 | −0.55547 | −1.10265 |
| 19 | −0.55066 | −1.10264 | −0.55148 | −1.10263 | −0.55256 | −1.10262 |
| 20 | −0.54822 | −1.10259 | −0.54896 | −1.10258 | −0.54994 | −1.10256 |
| Mean | −0.56636 | −1.10277 | −0.56778 | −1.10276 | −0.56969 | −1.10276 |
| Deviation | 0.01406 | 0.00016 | 0.01465 | 0.00015 | 0.01544 | 0.00015 |

**Table 4.** Dependence of the sample mean energy on the orbital exponent. All the results were obtained for a sampling region defined by $10.0 \leq r \leq 23.0$ bohr and $0.0 \leq \theta \leq 90.0°$. See the text for additional details

| Orbital exponent | Number of points | SR | | LCAO | |
|---|---|---|---|---|---|
| | | Energy | Standard deviation | Energy | Standard deviation |
| 0.90 | 11,921 | −1.10272 | 0.00014 | −0.47414 | 0.01666 |
| 0.95 | 11,921 | −1.10269 | 0.00019 | −0.51704 | 0.01581 |
| 1.00 | 11,921 | −1.10261 | 0.00036 | −0.56244 | 0.01496 |
| 1.05 | 11,921 | −1.10242 | 0.00083 | −0.61033 | 0.01410 |
| 1.10 | 11,686 | −1.10214 | 0.00152 | −0.66106 | 0.01317 |
| 1.15 | 10,749 | −1.10225 | 0.00124 | −0.71528 | 0.01193 |
| 1.20 | 9,873 | −1.10235 | 0.00100 | −0.77180 | 0.01074 |
| 1.25 | 9,035 | −1.10245 | 0.00079 | −0.83065 | 0.00960 |
| 1.30 | 8,220 | −1.10254 | 0.00059 | −0.89185 | 0.00851 |
| 1.35 | 7,399 | −1.10262 | 0.00042 | −0.95542 | 0.00747 |
| 1.40 | 6,493 | −1.10271 | 0.00027 | −1.02145 | 0.00648 |
| 1.45 | 5,019 | −1.10282 | 0.00015 | −1.09048 | 0.00545 |
| 1.4815 | 4,935 | −1.10281 | 0.00015 | −1.13416 | 0.00511 |
| 1.50 | 5,217 | −1.10278 | 0.00019 | −1.15982 | 0.00507 |

**Table 5.** Local values of the kinetic energy contribution of the starting function to the electronic energy

| Orbital exponent | Starting function | Contribution | Energy |
|---|---|---|---|
| 1.00 | 0.00487 | −0.9036166 | −1.10310 |
| 1.05 | 0.00317 | −0.9036215 | −1.10310 |
| 1.10 | 0.00206 | −0.9036214 | −1.10310 |
| 1.15 | 0.00133 | −0.9036223 | −1.10311 |
| 1.20 | 0.00086 | −0.9036223 | −1.10311 |
| 1.25 | 0.00055 | −0.9036222 | −1.10311 |
| 1.30 | 0.00035 | −0.9036225 | −1.10311 |
| 1.35 | 0.00023 | −0.9036225 | −1.10311 |
| 1.40 | 0.00014 | −0.9036224 | −1.10311 |
| 1.45 | 0.00009 | −0.9036224 | −1.10311 |
| 1.50 | 0.00006 | −0.9036223 | −1.10311 |

**Table 6.** Predicted total energies for different bond lengths. All the results were obtained for a sampling region defined by $10.0 \leq r \leq 23.0$ bohr and $0 \leq \theta \leq 90°$. See Ref. [4] for the exact energies

| $R$ | Predicted | Exact | $R$ | Predicted | Exact |
|---|---|---|---|---|---|
| 1.0 | −0.45157 | −0.45178 | 3.2 | −0.57086 | −0.57074 |
| 1.2 | −0.52648 | −0.52897 | 3.4 | −0.56432 | −0.56408 |
| 1.4 | −0.56813 | −0.56998 | 3.6 | −0.55787 | −0.55771 |
| 1.6 | −0.59085 | −0.59093 | 3.8 | −0.55189 | −0.55170 |
| 1.8 | −0.60020 | −0.60025 | 4.0 | −0.54628 | −0.54608 |
| 2.0 | −0.60261 | −0.60263 | 4.2 | −0.54113 | −0.54090 |
| 2.2 | −0.60084 | −0.60083 | 4.4 | −0.53639 | −0.53615 |
| 2.4 | −0.59658 | −0.59654 | 4.6 | −0.53209 | −0.53183 |
| 2.6 | −0.59089 | −0.59083 | 4.8 | −0.52820 | −0.52793 |
| 2.8 | −0.58443 | −0.58435 | 5.0 | −0.52471 | −0.52442 |
| 3.0 | −0.57766 | −0.57756 | 10.0 | −0.50141 | −0.50058 |

**Table 7.** Electronic energies obtained for different input energies

| Input energy | Predicted energy | Input energy | Predicted energy |
|---|---|---|---|
| −0.90 | −0.90009 | −1.10 | −1.09998 |
| −1.00 | −1.00003 | −1.10263 | −1.10261 |
| −1.05 | −1.05001 | −1.15 | −1.14996 |
| −1.06 | −1.06000 | −1.20 | −1.19993 |

different energies should be tested but this step was omitted because at this moment we are determining whether the SR formulation works as expected.)

The local values, at some chosen points of that sampling region, for the ratio $\Psi_{SR}/\Psi_{acc}$ of the predicted SR function over the accurate function of Weinhold and Chinen [5] are shown in Table 3. For this comparison all the values of the predicted function were multiplied by the same constant in order to show more clearly the similarity in the behaviour of both functions; the value of the constant is the one that brings into concordance the values of the functions at the first point.

The results obtained at the equilibrium bond length and using the exact energy as an input when varying the orbital exponents of the two atomic orbitals are collected in Table 4. Although the same sampling region is used in all cases, the number of points at which the calculation is successful decreases as the orbital exponent is increased: the orbitals become more and more contracted as one progresses through the table and the calculation fails because the values of the starting function become extremely small towards the tail of the $r$ interval. The interesting point in this table is the quasiconstancy of the mean SR energy compared with the strong variation in the mean LCAO energy. This is the result expected from the SR formulation. For completeness, the result obtained for the value 1.4815 of the orbital exponent is included. This is the optimum value obtained by Weinhold and Chinen [5], which yields a total energy of −0.60262 hartree, while the SR value is −0.60281 hartree.

Another interesting point to be mentioned in connection with the previously described calculations is the adjustment of the correction function to the new situation produced by a change in the orbital exponents. As an example, the local values obtained at $r = 10.0$ bohr and $\theta = 90°$ for the starting function, its contribution to the kinetic energy, and the predicted electronic energy are presented in Table 5. Before commenting on those values, it is appropriate to mention that, although the expectation value of the kinetic energy (as obtained in a variational calculation) must be positive, the local values of the kinetic energy may be either positive or negative. As observed in this table, the starting function changes considerably as the orbital exponents are increased; however, the kinetic energy contribution to the electronic energy remains constant to five significant figures. This result indicates that the correction function has also changed appropriately, so the kinetic energy contributions of both functions remain unchanged, taking into account that, to five significant figures, the predicted local electronic energy remains constant.

It remains to test whether the sampling region is appropriate for different bond lengths. The confirmation may be found first in the results presented in Table 6, obtained using as an input at each bond length the corresponding exact energy [4]. In this table one can observe the excellent agreement between the mean SR energy and the exact energy (i.e., the input energy). In addition, the hypothesis that the SR function reproduces the accurate function was tested using the sample mean of the ratio of the predicted SR function over the accurate function of Weinhold and Chinen [5], $\Psi_{\mathrm{SR}}/\Psi_{\mathrm{acc}}$. The results (not presented here for simplicity) for the standard deviation and the confidence interval (evaluated at a 99% level of confidence, using Student's [6] formulation) for the mean confirm the hypothesis for all the bond lengths considered. (For simplicity in the comparison of the results, the sample mean of the ratio obtained at each bond length was multiplied by an appropriate factor in order to make it equal to 1.0, with the corresponding standard deviations and confidence intervals modified appropriately.)

An interesting point to be mentioned in connection with Table 6 is the fact that SR calculations will predict the correct dissociation behaviour while density functional theory calculations fail in that regard for one-electron molecular systems, as discussed recently [7].

All the preceding calculations were performed using as inputs the correct energies and now we proceed with a predictive calculation. Calculations were performed for the complete sampling region (with 11921 points), with input energies ranging from $-0.9$ to $-1.2$ hartree, and the corresponding results are presented in Table 7. It may be observed in this table that concordance between the input energy and the sample mean is obtained for $E_i = -1.06$ hartree. The standard deviation for the mean energy is 0.00034 and the mean ratio of the predicted function over the accurate function of Weinhold and Chinen [5] is $1.0 \pm 0.02183$ (at a 99% level of confidence). The error with respect to the exact energy is 3.87%.

On the other hand, the mean energy for the starting function is $-0.56244$ hartree, with a standard deviation of 0.01496 and an error with respect to the correct energy of 49.0%, showing clearly the improvement introduced by the SR formulation.

## 4 Conclusions

The numerical evidence presented indicates that the appropriate sampling region to be used in SR calculations should be one in which the starting function has small local values, which means working in its tail region. The characteristic to be observed in an appropriate sampling region is a quasiconstancy of the local SR energies, in contrast to the variation of the local energies of the starting function. This difference in behaviour will provide clear indication of the improvement introduced by the SR formulation.

The acceptance of a mean energy as an estimate of the correct energy should be based on its standard deviation, with the added condition that the input energy should lie within (or close enough to) the confidence interval of the mean energy.

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