The rotating Morse potential model for diatomic molecules in the $J$-matrix representation: II. The $S$-matrix approach

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Abstract
This is the second article in which we study the rotating Morse potential model for diatomic molecules using the tridiagonal $J$-matrix approach. Here, we further improve the accuracy of computing the bound states and resonance energies for this potential model from the poles of the $S$-matrix for arbitrary angular momentum. The calculation is performed using an infinite square integrable basis that supports a tridiagonal matrix representation for the reference Hamiltonian, which is included in the computations analytically without truncation. Our method has been applied to both the regular and inverted Morse potential with favourable results in comparison with available numerical data. We have also shown that the present method adds a few significant digits to the accuracy obtained from the finite dimensional approach (e.g. the complex rotation method). Moreover, it allows us to easily handle both analytic and non-analytic potentials as well as $1/r$ singular potentials.

It is well known that the Morse potential model describes very well the vibrations of diatomic molecules [1]. This is because such systems can be modelled by two positive charges (the two atomic nuclei) that produce the Coulomb potential in which the electronic cloud moves. A similar type of modelling was also applied to nuclear molecules [2]. However, in this case there are no well-defined centres and the potential in which the nucleons move arises from the sum of interaction between all nucleons. In the language of energy scales, the electronic excitation energy, the vibration energy and the rotational molecular energy for diatomic molecules are widely separated energy scales, hence making the three degrees of freedom completely uncoupled. For a nuclear molecule, on the other hand, the single nucleon excitation and rotational energies are comparable for even the lowest angular momentum. Thus, it is expected that the energy associated with vibrations of the inter-nuclear coordinates will also be of the same order of magnitude. This will lead to a more complex energy spectrum reflecting the much stronger coupling among the intrinsic, vibrational and rotational degrees of freedom of nuclear molecules.

The Morse potential is an element in the class of potentials for which an analytic solution of the Schrödinger equation exists for zero angular momentum [3]. It is written as

$$V_M(r) = V_0 [e^{-2\alpha(x-1)} - 2e^{-\alpha(x-1)}], \quad x = r/r_0,$$

where $V_0$ is the strength of the potential (or the dissociation energy in the context of diatomic molecules), $r_0$ is the equilibrium intermolecular distance and $\alpha$ is a positive number controlling the decay length of the potential. For $V_0 > 0$, this potential has a minimum of $-V_0$ at $r = r_0$ and it is called the regular Morse potential. For $V_0 < 0$, it has a maximum of $-V_0$ there and it is called the inverted Morse potential. Asymptotically (as $r$ becomes very large), it goes to zero. The rotating Morse potential is the sum of the repulsive centrifugal potential barrier, $\hbar^2 \ell(\ell+1)/2m r^2$, and the Morse potentials (1). Generally, this effective potential shows a valley followed by a potential barrier which will then have two major effects. For the inverted Morse potentials where $V_0 < 0$, some resonances will be developed and the number of bound states will be reduced as $\ell$ increases. There will also be a critical angular momentum value, $\ell_c$, beyond which no bound states
are found and this critical value will depend on the potential parameters \( V_0 \) and \( \alpha \). Many numerical approaches using various approximation techniques have been proposed for solving the rotating Morse potential. These were extensively implemented with varying degrees of accuracy and stability [4]. Other semi-analytic methods have also been used such as the Nikiforov–Uvarov method [5] and the asymptotic iteration methods [6].

In our previous work [7], we have used the tridiagonal representation approach inspired by the \( J \)-matrix method [8] to compute the bound state energy spectrum of four different types of diatomic molecules: \( \text{H}_2 \), \( \text{LiH} \), \( \text{HCl} \) and \( \text{CO} \). Our approach provided an alternative method for obtaining the bound state energies for these diatomic molecules with improved accuracy and could easily be extended to other molecules. The numerical results have been favourably compared with those obtained using other approximation schemes [4]. In this work, we extend the approach to handle not only the bound states but also resonances associated with the rotating Morse potential model.

The direct way to compute the resonances is based on the accurate definition of the resonances as being the poles of the scattering \( S \)-matrix in the complex energy plane. One can show that each element of the \( S \)-matrix is singular at the complex resonance energy \( E \):

\[
S^{-1}(E) = 0, \quad E = E_R \pm iE_I. \tag{2}
\]

This condition is sufficient for obtaining the resonance position \( E_R \) and width \( \Gamma = 2E_I \). Several methods to find the complex resonance energies of a given scattering Hamiltonian are available. There are many techniques that enable us to evaluate the \( S \)-matrix. One such approach is to use the Jost function and its analytic properties [9]. In another approach, Yamani and Abdelmonem [10] showed how to calculate the \( S \)-matrix at the real Harris energy eigenvalues, and subsequently perform analytic continuation of the \( S \)-matrix to the complex energy plane. The required resonance information is then extracted from the analytically continued \( S \)-matrix. In our present work, we will evaluate the resonances and bound state energies associated with the rotating Morse potential by combining the properties of the \( S \)-matrix, the complex rotation method [11], and the analytical and computational power of the \( J \)-matrix method [8]. In our previous work [7], we have restricted our calculation to a finite dimensional subspace spanned by a subset of the \( J \)-matrix square integrable basis. Due to the finiteness of the dimensional space, the accuracy of our numerical results is somewhat limited. Any additional improvement requires larger spaces, and consequently more computational time and less stability. Since the objective is to increase the accuracy and improve the efficiency in locating the resonance positions and widths without extending too much the computing time or reducing numerical stability, in the present work we have opted to use the analytic power of the \( J \)-matrix approach. It will enable us to include, without truncation, all of the exactly solvable part of the Hamiltonian as an infinite tridiagonal matrix tail (usually referred to as the \( H_0 \) problem in the \( J \)-matrix literature). For the present problem, \( H_0 \) is just the kinetic energy operator (i.e. the sum of the second-order radial differential operator and the orbital term).

Direct study of resonances is usually done in the complex energy plane. Resonance energies are the subset of the poles of the \( S \)-matrix which are located in the lower half of the complex energy plane. One way to uncover these resonances, which are ‘hidden’ below the real line in the complex \( E \)-plane, is to use the complex scaling (complex rotation) method [11]. This method exposes the resonance poles and makes their study and manipulation easier. The subset of eigenvalues that corresponds to resonance and bound states spectra remain stable against variations in all computational parameters.

The time-independent Schrödinger wave equation for a point particle in a spherically symmetric potential \( V(r) \) reads as follows:

\[
(H - E) \chi = \left[ -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\ell(\ell + 1)\hbar^2}{2mr^2} + V(r) - E \right] \chi = 0, \tag{3}
\]

where \( \chi(r) \) is the wavefunction which is parameterized by the potential parameters, \( \ell \) and \( E \). We expand \( \chi \) in an \( L^2 \) complete basis set \( \{ \phi_n \} \) which is chosen to make the matrix representation of the reference Hamiltonian, \( H_0 \equiv H - V \), tridiagonal. The basis is parameterized by a positive length scale parameter \( \lambda \) as \( \{ \phi_n(\lambda r) \} \), which also allows for more computational freedom. The following choice of basis functions [12] is compatible with the domain of the Hamiltonian, satisfies the desired boundary conditions and results in a tridiagonal matrix representation for \( H_0 \):

\[
\phi_n(r) = a_n (\lambda r)^{\nu+1} e^{-r/2} L_n^\nu(x), \quad n = 0, 1, 2, \ldots, \tag{4}
\]

where \( x = \lambda r \) and \( \nu = 2\ell + 1 \) in the ‘Laguerre basis’, whereas \( x = (\lambda r)^{2} \) and \( \nu = \ell + \frac{1}{2} \) in the ‘oscillator basis’. \( L_n^\nu(x) \) is the Laguerre polynomial of degree \( n \) and \( a_n \) is the normalization constant given in [7] for both bases. The reference Hamiltonian \( H_0 \) in this representation, which is at the heart of the \( J \)-matrix approach, is accounted for in full. On the other hand, the short-range Morse potential \( V \) is approximated by its matrix elements in an adequate subset of the basis using the Gauss quadrature approach [13]. That is, the matrix representation of the full Hamiltonian becomes

\[
H_{nm} = \begin{cases} 
(H_0)_{nm} + V_{nm}, & n, m \leq N - 1 \\
(H_0)_{nm}, & n, m > N - 1.
\end{cases} \tag{5}
\]

Such a representation is the fundamental underlying feature of the \( J \)-matrix [8] method. As is obvious from (5), the reference Hamiltonian, which includes the orbital term, is not truncated as is usually done in the finite calculation methods. This full account of the reference Hamiltonian should result in a substantial improvement on the accuracy of the results especially for large angular momenta. This constitutes the real power of the \( S \)-matrix approach that we propose. Moreover, in finding resonances and bound state energies we use the ‘direct method’ based on the \( J \)-matrix calculation of the scattering matrix in the complex energy plane. Bound states are associated with negative real poles of the \( S \)-matrix while resonances are associated with complex
Table 1. The explicit form of the kinematic quantities $T_0(E)$, $R^\pm(E)$, $J_{N-1,N}(E)$ and $D^N_v$ in both Laguerre and oscillator bases. The three-term recursion relations for $s_n$ and $c_n$ (collectively shown as $f_n$) in both bases are also given.

| Laguerre basis | Oscillator basis |
|----------------|------------------|
| $T_0(E)$       | $s_0 = \frac{\sqrt{\pi}}{\Gamma(\nu+1)} e^{-E/2} x^{(\nu+1)/2}, \quad x = 2E/\lambda^2$ |
| $R^\pm(E)$     | $c_0 = \frac{\sqrt{\pi}}{\Gamma(\nu+1)} e^{-E/2} x^{-(\nu+1)/2}; \quad F_1(-v, 1 - v; x)$ |
| $J_{N-1,N}(E)$ | $s_1 = -\frac{\sqrt{\pi}}{\Gamma(\nu+1)} (v + 1 - x) x^{-(\nu+1)/2}; \quad F_1(-v, 1 - v; x)$ |
| $D^N_v$        | $c_1 = -\frac{\sqrt{\pi}}{\Gamma(\nu+1)} e^{-E/2} x^{(\nu+1)/2}; \quad F_1(-v, 1 - v; x)$ |
| Recursion relation | \(
\begin{align*}
T_n &= \frac{c_n - i \lambda_n}{c_n + i \lambda_n}, \quad R^\pm_n = \frac{c_n \pm i \lambda_n}{c_{n+1} \pm i \lambda_{n+1}},
\end{align*}
\)
| \begin{align*}
|S| &= \sum_{n=0}^{\infty} s_n |\phi_n\rangle, \quad |C| = \sum_{n=0}^{\infty} c_n |\phi_n\rangle,
|S| &= \sum_{n=0}^{\infty} s_n |\phi_n\rangle, \quad |C| = \sum_{n=0}^{\infty} c_n |\phi_n\rangle,
\end{align*}
Similar negative energy resonances were discussed in Table 4.

Table 2. Bound and resonance energies calculated using the S-matrix approach in the Laguerre basis for the inverted Morse potential with the parameters: $V_0 = -6 \text{ fm}^{-2}$, $\alpha = 0.3 \text{ fm}^{-1}$, $r_0 = 4.0 \text{ fm}$ and $\ell = 0$.

| $N$ | $\lambda$ | $E = E_R - i E_I$ (fm$^{-2}$) | Rawitscher [15] |
|-----|-----------|--------------------------------|-----------------|
| 25  | 25        | -8.108 988 161 869             | -8.1090         |
| 30  | 35        | 1.177 806 385 671 - i2.01 $\times 10^{-13}$ | 1.1783         |
| 35  | 40        | 5.625 155 807 690 - i0.035 131 892 716 | 5.625 16 - i0.035 1319 |
| 45  | 40        | 6.891 102 707 478 - i1.319 371 415 391 |                |
| 50  | 40        | 7.318 247 116 408 - i3.588 665 807 635 |                |
| 50  | 45        | 7.111 103 616 788 - i6.071 543 045 928 |                |
| 55  | 50        | 6.362 668 116 127 - i8.600 530 465 794 |                |
| 60  | 50        | 5.144 646 234 924 - i11.095 956 159 76 |                |
| 60  | 50        | 3.512 295 278 617 - i13.515 139 458 24 |                |
| 75  | 65        | 1.509 512 035 105 - i15.833 428 961 53 |                |
| 75  | 65        | -0.287 814 446 009 - i18.035 823 158 14 |                |
| 75  | 70        | -3.469 692 551 465 - i20.112 763 088 40 |                |
| 75  | 70        | -6.390 695 228 08 - i22.057 876 121 32 |                |
| 85  | 80        | -9.569 070 644 38 - i23.866 747 6308 |                |
| 85  | 80        | -12.986 084 802 - i25. 536 250 88 |                |
| 85  | 80        | -16.625 492 - i27.064 165 |                |

Table 3. Reproduction of table 2 but for $\ell = 1$.

| $N$ | $\lambda$ | $E = E_R - i E_I$ (fm$^{-2}$) |
|-----|-----------|--------------------------------|
| 30  | 30        | -1.812 991 439 373             |
| 35  | 35        | 4.343 378 629 186 - i0.000 086 853 698 |
| 45  | 40        | 6.665 073 438 079 - i0.531 572 234 93 |
| 55  | 45        | 7.364 866 543 876 - i12.568 333 087 462 |
| 65  | 50        | 7.436 775 874 472 - i14.992 463 411 191 |
| 75  | 55        | 6.935 679 941 774 - i17.522 073 704 643 |
| 80  | 60        | 5.938 612 579 913 - i10.047 943 002 88 |
| 80  | 60        | 4.506 823 029 849 - i12.513 888 969 73 |
| 80  | 60        | 2.688 440 123 933 - i14.887 642 141 49 |
| 80  | 60        | 0.522 010 509 971 - i17.149 522 987 28 |
| 80  | 60        | -1.960 934 522 180 - i19.287 108 917 84 |
| 80  | 60        | -4.734 098 232 106 - i21.292 423 021 18 |
| 80  | 60        | -7.775 172 363 055 - i23.160 327 814 47 |
| 80  | 60        | -11.064 951 097 97 - i24.887 549 343 39 |

Table 4. Bound and resonance energies calculated using the S-matrix approach in the oscillator basis for the following Morse potential parameters (in the units $\hbar = m = 1$): $V_0 = -10$, $\alpha = 2.0$, $r_0 = 1.0$ and $\ell = 2$.

| $N$ | $\lambda$ | $E = E_R - i E_I$ (au) |
|-----|-----------|-------------------------|
| 70  | 10        | -30.413 8814            |
| 70  | 8         | 10.926 0145 - i0.302 741 |
| 70  | 8         | 17.123 950 - i1.502 698 |
| 70  | 8         | 11.052 057 - i12.190 569 |
| 80  | 9         | -5.037 642 - i52.540 664 |

application in ultra-cold atomic collisions at negative energies [16]. Similar negative energy resonances were discussed in the past by one of the authors [17]. In table 3, we show the results of our calculation using the same parameters as in table 2 but with nonzero angular momentum ($\ell = 1$). Additionally, in table 4, we use the oscillator basis and choose a different set of model parameters (in atomic units) and for $\ell = 2$.

The numerical results for the resonances and bound states shown in tables 2–4, which are generated by the S-matrix approach, are very close to those obtained by complex rotation. Hence, the effect of the infinite tail resulting from the J-matrix approach for this model has no substantial contribution. On the other hand, we expect that the infinite tail originating from the $H_0$ contribution will be more important for higher values of the angular momentum and/or a shorter potential range (large $\alpha$). To study quantitatively the tail effect, we use the following numerical approximation for the Hamiltonian

$$H_{nm} \approx \left( (H_0)_{nm} + V_{nm}, \quad m, n \leq N - 1 \right)$$

which restricts the potential contribution to an $N \times N$ subspace while the $H_0$ part of the Hamiltonian is extended to $(N + M) \times (N + M)$ space to allow for an extra $M$-dimensional tridiagonal tail contribution from $H_0$. In the S-matrix approach, this tail goes to infinity but we will see numerically that the tail contribution in our model reaches its asymptotic contribution very quickly. Specifically, the asymptotic limit is already reached for $M = 10$. Figure 1 shows the results of resonance calculations with the parameters (in atomic units $\hbar = m = 1$): $V_0 = -10$, $r_0 = 1$, $\alpha = 0.5$ and $\ell = 5$ using the Laguerre basis with $\lambda = 15$ and $\theta = 0.9$ radians. First, we computed the resonances associated with this potential for a large value of $N$ ($N = 100$ and $M = 0$) shown as crosses in figure 1 where they serve as a reference for comparison to the values generated with smaller values of $N$ and increasing length of the tail. We note from the figure that the tail effect is more pronounced for deep resonances. A similar analysis can be done by looking at the numerical values in a tabular form for these resonances in the presence of a tail, which shows that the tail effect is really confined to improving the last couple of digits.

In summary, we extended our approach in [7] to the computation of the bound states and resonance energies, as being the poles of the $S$-matrix, using the power of the $J$-matrix technique that includes a partial contribution of the potential but full analytic contribution of the reference Hamiltonian. Our approach could easily be generalized to handle other short-range and even $1/r$ singular potentials such as the Yukawa and Hulthén potentials, to mention only a few [18]. These results suggest that our present approach is of comparable accuracy to the complex rotation approach. However, the $J$-matrix
Figure 1. Resonance plots identified with the pair \((N, M)\), where \(N\) is the size of the potential matrix and \(N + M\) is the size of the \(H_0\) matrix. The crosses show the most accurate location of the resonances (corresponding to \(N = 100\) and \(M = 0\)). The grid scale is 10 energy units (\(V_0\) units).

(This figure is in colour only in the electronic version)

approach can easily handle non-analytic and \(1/r\) singular potentials, which cannot be handled with great accuracy using other approaches and cannot be handled easily using the complex rotation method. We have also studied the importance of the tail contribution inherent in the \(J\)-matrix approach and showed that the tail effect will improve the accuracy of the resonances by a few significant digits for the present model.

In the forthcoming third article of this series, we will investigate a generalized three-parameter Morse potential model that should be more suitable and give a higher degree of freedom for the description of various diatomic molecules. This three-parameter Morse potential reads as follows:

\[
V_{GM}(r) = V_0 \left[ e^{-2\alpha(r - r_0)/r_0} - 2\beta e^{-\alpha(r - r_0)/r_0} \right],
\]

where \(\beta\) is a new dimensionless parameter whose value is unity for the regular Morse potential. As shown in paper I, this generalized potential results in an exact \(S\)-wave (\(\ell = 0\)) solution for the time-independent Schrödinger equation.

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