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Vibrational–Rotational Structure of Supersingular Plus Coulomb Potential $A/r^4 - Z/r$*

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The vibrational–rotational states of the supersingular plus Coulomb potential $A/r^4 - Z/r$ are variationally constructed using a nonorthogonal basis of atomic hydrogenic eigenfunctions modulated by an exponential factor $\exp(-\alpha/r)$, ensuring the correct behavior in the vicinity of the supersingularity. The construction is carried out in two successive stages. The first stage is restricted to trial functions without radial nodes, leading to a variational optimization of the parameters of the basis for each value of the angular momentum. The second stage uses the complete basis to construct linear trial functions and to formulate the variational problem in terms of secular equations, yielding the successive vibrational and rotational states. Numerical results for the corresponding energy levels are presented for different combinations of the intensity parameters of the potential.

1. INTRODUCTION

Zare in his early work to explain the vibrational structure of the visible spectrum of molecular iodine associated with the transitions $B^3\prod_{0^+u} \rightarrow X^1\sum_{0^+g}$ (Zare, 1964), and Zare *et al.* (1965), in their corresponding investigation of five band systems of molecular nitrogen, used the Rydberg–Klein–Reese method to construct the potential functions from the spectroscopic data (Klein, 1932; Reese, 1947; Rydberg, 1931). They extended the potential curves beyond the central range covered by such data, through a smooth joining with repulsive and attractive segments of the form

$$V_{\text{rep}} = \frac{a}{r^{12}} + b \tag{1}$$

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$$V_{\mathrm{att}} = \frac{a'}{r^{b'}} \tag{2}$$

These extrapolated portions of the potential are important for the subsequent numerical integration of the Schrödinger equation. Here, we want to call the reader's attention to the supersingular nature of the small separation portion of Eq. (1); potentials of the form $1/r^{\alpha}$ are classified as supersingular for $\alpha > 2.5$ (Detwiler and Klauder, 1975; Ezawa *et al.*, 1975; Harrel, 1977; Klauder, 1973, 1978).

Of course, the supersingular behavior of the potential functions describing molecular interactions was recognized very early on, as illustrated by the general $m - n$ Mie potential (Mie, 1903),

$$V_M(r) = \varepsilon\left[\frac{m}{n-m}\left(\frac{r_0}{r}\right)^n - \frac{n}{n-m}\left(\frac{r_0}{r}\right)^m\right] \tag{3}$$

and the well-known 6–12 Lennard-Jones potential (Lennard-Jones, 1924). In contrast the quantum mechanical studies of supersingular potentials are relatively recent (Fernández, 1991; Guardiola and Ros, 1992; Solano-Torres *et al.*, 1992; Znojil, 1984, 1991, 1992), some of which have focused on perturbative expansions of the ground state. More recently, such studies for the so-called spiked oscillator

$$V_{\text{sp–o}}(r) = \frac{\lambda}{r^{\alpha}} + r^2 \tag{4}$$

were performed variationally, still for the ground state only, for $\alpha = 5/2$ (Aguilera-Navarro and Ullah, 1994) and $\alpha = 4$ (Aguilera-Navarro *et al.*, 1994). In a very recent work, the vibrational–rotational energy levels of the spiked oscillator with $\alpha = 4$ were variationally analyzed (Aguilera-Navarro and Ley-Koo, 1997), recognizing the need of a systematic investigation of the vibrational–rotational structure of supersingular potentials.

This work consists of a variational analysis of the vibrational–rotational structure of the supersingular plus Coulomb potential,

$$V_{\mathrm{SC}}(r) = \frac{A}{r^4} - \frac{Z}{r} \tag{5}$$

which in the notation of Eq. (3) is identified as a 1–4 Mie potential. In the next section the variational analysis is formulated using variational trial functions constructed as linear superpositions of atomic hydrogenic eigenfunctions modulated by an exponential factor $\exp(-\alpha/r)$, which ensures the correct behavior close to the supersingularity $r \to 0$. The variational analysis of the vibrational–rotational structure of the potential is carried out in two successive stages. The first stage is restricted to trial functions without radial nodes, leading to the optimization of the parameters of the functions of the basis for each value of the angular momentum, through the minimization of the energy of the corresponding states. The second stage uses the complete basis for the construction of linear trial functions and the formulation of the variational problem in terms of secular equations, yielding the variational solutions for the states with successive vibrational and rotational excitations. Since the functions of the basis are not orthogonal, due to the presence of the modulation factor, the matrix formulation of the eigenvalue problem must take such a nonorthogonality into account (Löwdin, 1950). Numerical results for the variational energies of the lowest vibrational–rotational states are presented in section 3 for a fixed value of $Z = 1$ and different values of the parameter A. The discussion deals with the validity of this type of trial function, and the prospects of its use in the study of other supersingular potentials.

2. LINEAR VARIATIONAL ANALYSIS

The radial Schrödinger equation to be solved is written as

$$\left[-\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} + \frac{\ell(\ell+1)}{r^2} + \frac{A}{r^4} - \frac{Z}{r}\right]R(r) = E\,R(r) \tag{6}$$

The variational analysis uses the basis of functions

$$R_{n_r\ell}(r,\beta) = N_{n_r\ell}\, e^{-\alpha/r-\beta r/n} r^{\ell}\, M\left(-n_r; 2\ell+2; \frac{2\beta r}{n}\right) \tag{7}$$

where the reader can identify the atomic hydrogenic functions, with the charge parameter β and $n = n_r + \ell + 1$, multiplied by the exponential modulation factor. The elimination of the supersingular term in Eq. (6) is ensured if the parameter α takes the value

$$\alpha = \sqrt{A} \tag{8}$$

The functions of Eq. (7) form a complete basis, but not an orthogonal one because of the presence of the modulation factor.

As anticipated, the variational solution of Eq. (6) is formulated first using the functions of Eq. (7) without radial nodes, for which $n_r = 0$ and the confluent hypergeometric function M becomes one. In such a case the evaluation of the expectation value of the energy in Eq. (6) is straightforward with the result

$$E_{v=0,\ell}(\beta) = -\left(\frac{\beta}{\ell+1}\right)^2 - \frac{2\alpha\ell\left(\frac{\beta}{\alpha(\ell+1)}\right)^{3/2}K_{2\ell}\left(4\sqrt{\frac{\alpha\beta}{\ell+1}}\right)}{K_{2\ell+3}\left(4\sqrt{\frac{\alpha\beta}{\ell+1}}\right)} + \frac{2\left(\frac{\beta}{\ell+1}\right)^2K_{2\ell+1}\left(4\sqrt{\frac{\alpha\beta}{\ell+1}}\right) + (2\beta-Z)\sqrt{\frac{\beta}{\alpha(\ell+1)}}K_{2\ell+2}\left(4\sqrt{\frac{\alpha\beta}{\ell+1}}\right)}{K_{2\ell+3}\left(4\sqrt{\frac{\alpha\beta}{\ell+1}}\right)} \tag{9}$$

where the first term corresponds to the atomic hydrogen energy and the successive terms in the fraction involve the expectation values of the inverse powers of r, $1/r^p$ for $p = 3, 2, 1$, in terms of the modified Bessel functions associated with the integrals (Abramowitz and Stegun, 1965),

$$\int_0^\infty x^{\nu-1} e^{-\frac{\gamma}{x}-\delta x}\, dx = 2\left(\frac{\gamma}{\delta}\right)^{\nu/2} K_\nu(2\sqrt{\gamma\delta}) \tag{10}$$

The normalization integral in the denominator of Eq. (9) corresponds to $p = 0$. Equation (9) exhibits the explicit dependence of the energy of the states with no vibrational excitation $\nu = 0$ and successive rotational excitations $\ell = 0, 1, 2, \ldots,$ on the variational parameter β. According to the variational principle the best energies are the minimum energies obtained from

$$\frac{dE_{v=0,\ell}(\beta)}{d\beta} = 0 \tag{11}$$

The minimization of the energy and optimization of the variational parameter is accomplished in a personal computer using the Mathematica program (Wolfram, 1988) to obtain Eq. (11) from Eq. (9), for chosen values of Z, A, and ℓ, and solving numerically for β.

The linear variational solution of Eq. (6) for states with any vibrational and rotational excitations, $v = 0, 1, 2, \ldots;\ \ell = 0, 1, 2, \ldots,$ is constructed using the basis of Eq. (7).

$$R_{v\ell}(r) = \sum_{n_r=0}^{N} a_{vn_r} R^H_{n_r\ell}(r, \beta) \tag{12}$$

The nonorthogonality of the basis of Eq. (7) leads to the matrix form of the eigenvalue problem of Eq. (6)

$$Ha = ESa \tag{13}$$

where a is the column matrix formed by the eigenvector components a_{vn_r}, and S is the overlap matrix of the functions of Eq. (7). The explicit forms of the matrix elements are

$$\langle n'_r\ell \mid n_r\ell\rangle = N_{n'_r\ell}N_{n_r\ell} \sum_{s=0}^{n'_r}\sum_{t=0}^{n_r} \frac{(-n'_r)_s(-n_r)_t}{(2\ell+2)_s s!(2\ell+2)_t t!}\,\frac{(2\beta)^{s+t}}{n'^s n^t}$$
$$\times 2\left[\frac{2\alpha}{\beta\left(\frac{1}{n'}+\frac{1}{n}\right)}\right]^{(2\ell+3+s+t)/2} K_{2\ell+3+s+t}\left(2\sqrt{2\alpha\beta\left(\frac{1}{n'}+\frac{1}{n}\right)}\right) \tag{14}$$

where the diagonal matrix elements have the value of one, corresponding to the normalization integral, and the off-diagonal matrix elements have absolute values less than one.

$$\begin{aligned}\langle n_r'\ell|H|n_r\ell\rangle &= -\frac{\beta^2}{n^2}\langle n_r'\ell \mid n_r\ell\rangle - 2\alpha\ell\langle n_r'\ell|\frac{1}{r^3}|n_r\ell\rangle \\ &\quad + \frac{2\alpha\beta}{n}\langle n_r'\ell|\frac{1}{r^2}|n_r\ell\rangle + (2\beta - Z)\langle n_r'\ell|\frac{1}{r}|n_r\ell\rangle + I_{n_r'n_r} \end{aligned} \tag{15}$$

where

$$\begin{aligned}&\langle n_r'\ell|\frac{1}{r^p}|n_r\ell\rangle \\ &= N_{n_r'\ell}N_{n_r\ell}\sum_{s=0}^{n_r'}\sum_{t=0}^{n_r}\frac{(-n_r')_s}{(2\ell+2)_s s!}\frac{(-n_r)_t}{(2\ell+2)_t t!}\frac{(2\beta)^{s+t}}{n'^s n^t} \\ &\quad \times 2\left[\frac{2\alpha}{\beta\left(\frac{1}{n'}+\frac{1}{n}\right)}\right]^{(2\ell+3-p+s+t)/2} K_{2\ell+3-p+s+t}\left(2\sqrt{2\alpha\beta\left(\frac{1}{n'}+\frac{1}{n}\right)}\right)\end{aligned} \tag{16a}$$

and

$$\begin{aligned}I_{n_r'n_r} &= \frac{4\alpha\beta n_r}{n(\ell+1)}N_{n_r'\ell}N_{n_r\ell}\sum_{s=0}^{n_r'}\sum_{t=0}^{n_r}\frac{(-n_r')_s}{(2\ell+2)_s s!}\frac{(-n_r+1)_t}{(2\ell+3)_t t!}\frac{(2\beta)^{s+t}}{n'^s n^t} \\ &\quad \times \left[\frac{2\alpha}{\beta\left(\frac{1}{n'}+\frac{1}{n}\right)}\right]^{(2\ell+1+s+t)/2} K_{2\ell+1+s+t}\left(2\sqrt{2\alpha\beta\left(\frac{1}{n'}+\frac{1}{n}\right)}\right)\end{aligned} \tag{16b}$$

The determination of the energy eigenvalues and eigenvectors in Eq. (13) makes use of the diagonalization of the real symmetric overlap matrix S by an orthogonal matrix P,

$$PS\tilde{P} = d \tag{17}$$

yielding positive eigenvalues d_i. The eigenvalue problem becomes

$$(d^{-1/2}PH\tilde{P}d^{-1/2})(d^{1/2}Pa) = E(d^{1/2}Pa) \tag{18}$$

where the matrix to be diagonalized

$$H' = d^{-1/2}PH\tilde{P}d^{-1/2} \tag{19}$$

is real and symmetric, and the eigenvectors

$$\Psi' = d^{1/2}Pa \tag{20}$$

are the intermediate step to obtain the eigenvectors of Eq. (13)

$$a = \tilde{P}\, d^{-1/2}\, \Psi' \tag{21}$$

Equations (14)–(16) allow the numerical implementation of the construction and diagonalization of the matrices of Eqs. (17) and (18). The numerical results for the vibrational–rotational energies $E_{v\ell}$ from Eq. (18) are reported in the following section.

3. NUMERICAL RESULTS AND DISCUSSION

The numerical results of the optimization of the variational parameters of the modulated hydrogenic trial functions, and the associated energies for radially nodeless states are presented in Table I, for the fixed value of $Z = 1$ in Eq. (6) and the value of α from Eq. (8). The successive columns contain the intensity parameter A of the supersingular term, the orbital angular momentum quantum number ℓ, and the optimized values of the parameter β and the energies $E_{0,\ell}$ from Eqs. (9) and (11).

A systematic trend can be identified from the numbers in Table I. As the intensity parameter A of the supersingular term becomes smaller, the potential of our interest in Eq. (5) tends to the pure Coulomb potential. Correspondingly, the energy levels of the $\ell = 0, 1, 2$ states tend to the hydrogenic levels as A takes on smaller values; for $A = 0.0001$ they are quite close to the values -0.25, $-0.25/2^2$, and $-0.25/3^2$, characteristic of the hydrogen atom with a nuclear charge $Z/2$. Undoubtedly, the lower angular momentum states are the most affected by the presence of the supersingular term in the potential; its effect on the higher angular momentum states is increasingly diminished. This behavior is numerically

Table I. Successive Entries Correspond to Intensity Parameter A of the Supersingular Term, the Orbital Momentum Angular ℓ, the Optimized Parameter β from Eqs. (9) to (11), and the Best Energies $E_{0\ell}$ from the Same Eqs. (9)–(11)

A	ℓ	β	$E_{0\ell}$
0.0001	0	0.4910626869972242	−0.245416062
	1	0.5004090585713405	−0.062499543
	2	0.5001109015403303	−0.027777772
0.01	0	0.4417940838972697	−0.218082862
	1	0.5035416500133421	−0.062462114
	2	0.5010904177064952	−0.027777238
1.0	0	0.3112405646772868	−0.138325359
	1	0.5103795011960180	−0.060669475
	2	0.5092554676490551	−0.027729914
25	0	0.2089689867723217	−0.076567812
	1	0.4556304289578258	−0.050321472
	2	0.5222653550125408	−0.026972985
100	0	0.1715447244001531	−0.055953927
	1	0.4002444926046950	−0.042000510
	2	0.5140164787822753	−0.025583677

Table II. Energy Eigenvalues $E_{0\ell}$ from the Diagonalization of Eq. (18) from Matrices of Different Dimension $N \times N$, Illustrating the Convergence Pattern for $A = 0.0001$

N	E_{0s}	E_{0p}
1	−0.245416062122	−0.062499542953
10	−0.245474657314	−0.062499702318
15	−0.245493734657	−0.062499795263
20	−0.245499432819	−0.062499807825
25	−0.245500179211	−0.062499814278
30	−0.245501719251	−0.062499816655
35	−0.245501727189	−0.062499817461
40	−0.245501731237	−0.062499831625

reflected by the decreasing difference and increasing closeness of the charge parameter $\beta \to Z/2$, as $A \to 0$.

The convergence of the energy eigenvalues $E_{0,\ell}$ for $\ell = 0$ and 1, and $A = 0.0001$, obtained from the diagonalization of Eq. (18), is explicitly illustrated in Table II as the dimensions of the corresponding matrices increase. The numerical

Table III. Entries Correspond to the Intensity Parameter A of the Supersingular Term, and Linear Variational Energies $E_{v\ell}$ of the Successive Vibro-Rotational States

A	E_{0s}	E_{1s}	E_{2s}	E_{3s}
0.0001	−0.2455017	−0.0624851	−0.0277752	−0.0156232
0.01	−0.2210285	−0.0614360	−0.0273129	−0.0152913
1	−0.1495349	−0.0479544	−0.0217006	−0.0123192
25	−0.0870562	−0.0330160	−0.0157534	−0.0090969
100	−0.0638181	−0.0262348	−0.0131638	−0.0076754
A	E_{0p}	E_{1p}	E_{2p}	E_{3p}
0.0001	−0.0624998	−0.0277762	−0.0156239	−0.0099992
0.01	−0.0624742	−0.0277693	−0.0156213	−0.0099981
1	−0.0607221	−0.0272018	−0.0153681	−0.0098599
25	−0.0591760	−0.0238182	−0.0138866	−0.0090883
100	−0.0478551	−0.0209881	−0.0125968	−0.0071219
A	E_{0d}	E_{1d}	E_{2d}	E_{3d}
0.0001	−0.0277777729	−0.0156247253	−0.0099997412	−0.0069443361
0.01	−0.0277774	−0.0156242	−0.0099992	−0.0069441
1	−0.0277438	−0.0156089	−0.0099913	−0.0069393
25	−0.0270638	−0.0152925	−0.0098218	−0.0068381
100	−0.0256810	−0.0146659	−0.0094889	−0.0066413

construction of matrix elements of Eqs. (15) and (16), and the diagonalization of Eq. (18) were implemented with the Fortran program. The converged results for 40 × 40 matrices for the different values of the intensity parameter A, and the successive vibrational $v = 0, 1, 2, 3$ and rotational $\ell = 0, 1, 2$ quantum numbers are shown in Table III. The reader can check that the systematic trend of the $E_{0,\ell}$ eigenenergies, as A changes, recognized from Table I and described in the previous paragraph, is extended to the vibrationally and rotationally excited levels.

The modulation exponential factor in the basis of Eq. (7) has ensured the correct behavior of the trial function of Eq. (12) for $r \to 0$ in the present investigation. The study of other supersingular potentials must also ensure the proper behavior of the wave-function at short distances. If the supersingular potential in Eq. (6) is of the form A/r^n, a modulation factor $\exp(-\alpha/r^s)$ with $2s + 2 = n$, and $\alpha = \sqrt{A}/s$ will ensure such a behavior.

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