COMMENT

Comment on ‘Non-relativistic treatment of diatomic molecules interacting with generalized Kratzer potential in hyperspherical coordinates’

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Abstract

We argue that the textbook method for solving eigenvalue equations is simpler, more elegant and efficient than the asymptotic iteration method applied in Durmus (2011 J. Phys. A: Math. Theor. 44 155205). We show that the Kratzer potential is not a realistic model for the vibration–rotation spectra of diatomic molecules because it predicts the position of the absorption infrared bands too far from the experimental ones (at least for the HCl and H₂ molecules chosen as illustrative examples in that paper).

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In order to study the vibration–rotation motion of diatomic molecules in $N$ dimensions, Durmus [1] chose the Kratzer potential and solved the Schrödinger equation in hyperspherical coordinates by means of the asymptotic iteration method (AIM). He obtained the well-known results and as an illustrative and practical application of the model, he restricted himself to the only apparently relevant case $N = 3$ calculating some vibration–rotation energies for H₂ and HCl. In what follows, we contrast the AIM derivation of the main equations with the well-known and widely used textbook approach, and also compare the theoretical results for those molecules with experimental ones.

The starting point is the Schrödinger equation

$$\left(-\frac{\hbar^2}{2\mu} \nabla^2 + V(r)\right)\Psi(r) = E\Psi(r),$$  \hspace{1cm} (1)

where $\mu$ is the reduced mass of the molecule and $E$ is the vibration–rotation energy. As a ‘realistic’ model for the interaction between the nuclei, the author chose the Kratzer potential

$$V(r) = D_e \left(\frac{r - r_e}{r}\right)^2 + \eta,$$  \hspace{1cm} (2)
where \( r_\text{e} \) is the equilibrium internuclear separation and \( D_\text{e} \) is the molecular dissociation energy (misleadingly called intermolecular separation and dissociation energy between diatomic molecules, respectively, by the author in [1]). He made a curious distinction between the modified Kratzer potential \( \eta = 0 \) and the Kratzer potential \( \eta = -D_\text{e} \) which are just two alternative expressions of the same interaction with the energy origin shifted by \( \eta \). Without a plausible justification, he further argued that it is useful from a physical point of view to consider the general \( N \)-dimensional case where

\[
    r^2 = \sum_{j=1}^{N} x_j^2, \quad \nabla^2 = \sum_{j=1}^{N} \frac{\partial^2}{\partial x_j^2}.
\]

Since the potential is spherically symmetric, one can separate the Schrödinger equation (1) into its radial and angular parts, and by means of well-known transformations, the former is reduced to [1]

\[
y F''(y) + \left( \frac{2\gamma + N - 1 - 2\beta}{y} \right) F'(y) + \left[ 2\kappa - \beta \left( \frac{2\gamma + N - 1}{y} \right) \right] F(y) = 0, \quad (4)
\]

where

\[
    y = \frac{r}{r_\text{e}}, \quad \kappa = \frac{2\mu D_\text{e} r_\text{e}^2}{\hbar^2}, \quad \beta = \frac{2\mu r_\text{e}^2 (D_\text{e} - E + \eta)}{\hbar^2},
\]

\[
    \gamma = \frac{N - 2}{2} + \sqrt{\left( \frac{l + \frac{N - 2}{2} \right)^2}},
\]

and \( l = 0, 1, \ldots \) is the angular-momentum quantum number (called \( l_{N-1} \) in [1]). In order to solve this equation, Durmus [1] applied the AIM which is an iterative approach that gives results for \( n = 0, 1, \ldots \) where \( n \) labels the number of iterations. By inspection of the particular outputs \( \beta_0, \beta_1, \ldots \) one hopefully derives the value of \( \beta_n \) for an arbitrary number \( n \) of iteration steps and then the allowed energy \( E = E_\text{nl} \). With some more ingenuity, one realizes that \( F(y) \) is proportional to the confluent hypergeometric function \( _1F_1(\cdot) \).

This procedure offers little difficulty if one already knows the exact result beforehand which is actually the case here. Once we have the solution in terms of the confluent hypergeometric function, we easily rewrite it in terms of the associated Laguerre polynomials [1, 3].

Solving equation (4) is a textbook problem [2] and the widely known approach is faster, more elegant and efficient than the AIM. If we define \( y = \frac{z}{\beta} \), then \( w(z) = F\left(\frac{z}{\beta}\right) \) satisfies

\[
z w''(z) + \left( 2\gamma + N - 1 - z \right) w'(z) + \left[ \frac{\kappa}{\beta} - \left( \gamma + \frac{N - 1}{2} \right) \right] w(z) = 0
\]

that is a particular case of Kummer’s equation [3]

\[
z w''(z) + (b - z) w'(z) - a w(z) = 0.
\]

Kummer’s function can be expanded in a power-series

\[
    M(a, b, z) = \sum_{j=0}^{\infty} \frac{a_j z^j}{j! b_j}.
\]
where $\xi_j = \xi((\xi + 1)(\xi + 2) \ldots (\xi + j - 1)$ and $\xi_0 = 1$. It becomes a polynomial of degree $n$ when $a = -n$ and $b \neq -m$ ($m$ and $n$ positive integers). On comparing equations (6) and (7), we directly obtain

$$\beta_{nl} = \frac{\kappa}{n + \gamma + \frac{N-1}{2}}$$

(9)

and [3]

$$F_n(y) = M(-n, 2\gamma + N - 1, 2\beta y) = _1F_1(-n, 2\nu + N - 1; 2\beta y).$$

(10)

It is clear that one can derive the solution to equation (4) directly from comparison of the appropriate equations in a way that makes the AIM utterly unnecessary.

Durmus [1] did not show any physical application of the $N$-dimensional model except for the obvious case $N = 3$. Most curiously he showed results in the form of a table and figure for both $\eta = 0$ and $\eta = -D_c$. Apparently, he did not realize that both spectra are the same but for an energy shift that is irrelevant from a physical point of view. Suffice it to say that the physical observables are not affected by this shift.

Another curious fact is that in table 2 the author only showed the energies for $n \geq l = 0, 1, \ldots$. In the case of a diatomic molecule, to which the model is supposed to apply, $n$ is the vibrational quantum number $v$ and $l$ is the rotational quantum number $J$ so that such a selection of quantum numbers is of scarce utility from a spectroscopic point of view (one would expect increasing $J$ for a given $v$).

Durmus [1] argued that the Kratzer potential provides a realistic description of molecular vibrations, but it is far from true as discussed by Příva [4] who stated that ‘However, in its basic form, this function provides only a rather crude approximation for the molecular potential, and for this reason it has not been popular with spectroscopists’. In the first place, the Kratzer potential supports an infinite number of vibration–rotation levels which is not the case of actual diatomic molecules. In addition to it, it does not describe the spectrum correctly as we will show in what follows. From the vibration–rotation energies written in the usual spectroscopic way

$$E_{v,J} = -\frac{\kappa D_c}{\left[v + \frac{1}{2} + \sqrt{\kappa + (J + \frac{1}{2})^2}\right]^2},$$

(11)

we obtain the spectral lines in wavenumber units

$$\tilde{\nu} = \frac{E_{v',J'} - E_{v,J}}{hc}$$

(12)

according to the selection rules $\Delta v = \pm 1$ and $\Delta J = \pm 1$ [5]. The results in Durmus’ table 2 do not even allow us to obtain the P and R branches of the fundamental absorption band ($v = 0, v' = 1, J' = J \pm 1$) [5]. The first two entries for HCl in that table predict the center of this band to appear at $E_{1,0} - E_{0,0} = 0.1482$ eV or 1195 cm$^{-1}$. However, it is well known that the center of the fundamental band is located at $\tilde{\nu} = 2886$ cm$^{-1}$ [5], more than twice the value given by Durmus’ energies. It is not better for H$_2$ (theoretical $= 2715.7$ cm$^{-1}$, experimental $= 4160.2$ cm$^{-1}$) as expected from a model that no spectroscopist would take seriously.

Summarizing the main conclusions of this comment, we may say that the application of the AIM for solving the Schrödinger equation with the Kratzer potential is far from being the best strategy. One obtains the same expressions in a more direct, easy and elegant way by means of the standard textbook method [2]. In addition to it, since Durmus did not show any plausible physical application of the model to space dimensions other than $N = 3$ and the results for ordinary diatomic molecules are extremely poor, we conclude that the model is of scarce physical utility.
References

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