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Commentary: Solutions of the Schrodinger equation of the shifted screened Kratzer potential and its thermodynamic functions using the extended Nikiforov–Uvarov method

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A Commentary on
Solutions of the Schrodinger equation of the shifted screened Kratzer potential and its thermodynamic functions using the extended Nikiforov-Uvarov method

by Ibrahim N, Okorie US, Sulaiman N, Rampho GJ and Ramantswana M (2022) Solutions of the Schrodinger equation of the shifted screened Kratzer potential and its thermodynamic functions using the extended Nikiforov–Uvarov method. Front. Phys. 10:988279. doi: 10.3389/fphy.2022.988279

1 Introduction

In a paper presented recently in this journal, Ibrahim et al. [1] proposed the shifted screened Kratzer potential for the analysis of the spectra of diatomic molecules. After a suitable transformation of part of the potential energy function, they derived analytical expressions for the vibration–rotation eigenvalues by means of the Nikiforov–Uvarov method. Ibrahim et al. also calculated the canonical partition function and some thermodynamic functions. The purpose of this commentary is the analysis of their results. In Section 2, we summarize some relevant aspects of the potential energy function for a diatomic molecule and analyze the spectrum of the shifted screened Kratzer potential. We also discuss the calculation of the canonical partition function. Finally, in Section 3, we summarize the main results and draw conclusions.

2 The shifted screened Kratzer potential

We begin the discussion summarizing a few well-known properties of the interatomic potential $V(r)$ for a diatomic molecule. Commonly, $V(r \to 0) = \infty$ and $V(r)$ exhibits a minimum value at the interatomic equilibrium distance r_e given by $V'(r_e) = 0$. The dissociation energy is defined as $D_e = V(r \to \infty) - V(r_e)$, assuming that $V(r \to \infty)$ is finite. One of the simplest examples is given by the Kratzer potential

$$V^K(D_e, r_e, r) = -2D_e\left(\frac{r_e}{r} - \frac{r_e^2}{2r^2}\right) \tag{1}$$

that supports an infinite number of bound states with energies $E_{vj}^K(D_e, r_e)$, $v = 0, 1, \ldots$, and $J = 0, 1, \ldots$, where v and J are the vibration and rotation quantum numbers, respectively. The Schrödinger equation with the Kratzer potential is exactly solvable.

Ibrahim et al. [1] proposed the so-called shifted screened Kratzer potential,

$$V(r) = -2D_e\left(\frac{r_e}{r} - \frac{r_e^2}{2r^2}\right)\left(2\lambda + \gamma e^{-\alpha r}\right), \tag{2}$$

where λ and γ are "shifting parameters" that can be "adjusted as desired." We should add, provided that $2\lambda + \gamma e^{-\alpha r} > 0$ for all r. They claimed that D_e and r_e are the dissociation energy and equilibrium bond length, respectively (we will discuss this point further). After a suitable transformation of r^{-1} and r^{-2} and further application of the Nikiforov–Uvarov method, they obtained the eigenvalues E_{nl}, where n and l are "the radial and orbital angular momentum quantum numbers," respectively. According to Ibrahim et al., $n = 0, 1, \ldots, N_{\max}$, where "$N_{\max}$ is the maximum vibration quantum number."

One may think that this model offers five adjustable parameters: D_e, r_e, λ, γ, and α. However, if we rewrite it as

$$V(r) = -2D_e'\left(\frac{r_e}{r} - \frac{r_e^2}{2r^2}\right)\left(1 + \gamma' e^{-\alpha r}\right), D_e' = 2\lambda D_e, \gamma' = \frac{\gamma}{2\lambda}, \tag{3}$$

we realize that there are just four independent parameters: D_e', r_e, γ', and α.

We can easily derive some properties of the spectrum supported by the potential (2) without solving the Schrödinger equation. If we take into account that

$$V^K([2\lambda + \gamma]D_e, r_e, r) < V(r) < V^K(2\lambda D_e, r_e, r), \tag{4}$$

then we conclude that the true eigenvalues E_{vJ} of the Schrödinger equation with the potential (2) are bounded as

$$E_{vj}^K([2\lambda + \gamma]D_e, r_e) < E_{vJ} < E_{vj}^K(2\lambda D_e, r_e). \tag{5}$$

Since both the lower and upper bounds correspond to the infinite spectra of Kratzer potentials, we conclude that the potential (2) also supports an infinite number of states with negative energy eigenvalues. One may wonder why Ibrahim et al. obtained a finite number of bound states instead of an infinite number of them. The reason is the transformation.

$$\frac{1}{r} \approx \frac{\alpha}{1 - e^{-\alpha r}} \tag{6}$$

that is reasonable when r is close to the origin, but it completely changes the behavior of the potential at infinity. The infinite spectrum of $V(r)$ is due to the behavior of the potential as r^{-1} for large values of r, while the transformed potential exhibits a completely different behavior.

One may argue that the approximation (6) leads to reasonably accurate eigenvalues for small values of the vibration quantum number. However, the approach followed by Ibrahim et al. faces another serious shortcoming. Since

$$V'(r_e) = \lambda\alpha e^{-\alpha r_e}, \tag{7}$$

then r_e is not the equilibrium bond length, and consequently, D_e is not the dissociation energy. If, as it appears to be, Ibrahim et al. substituted experimental values for these parameters, the resulting curves are unsuitable for a physical application. There is something even more serious in the authors' paper. Figures 1–4 show the variation in E_{nl} for the molecules H_2, LiH, HCl, and CO with respect to D_e, r_e, α, and μ, respectively. Such an analysis is incomprehensible because a given set of those parameters defines one and only one molecule. In other words, it is incorrect, for example, to show E_{nl} for CO for different values of D_e because only one value of the dissociation energy is compatible with that molecule.

We can derive an approximate expression for r_e in terms of the true equilibrium bond length $\tilde{r}_e$ for the potential (2). If we solve $V'(\tilde{r}_e) = 0$ for r_e by means of a power series, we obtain

$$r_e = \tilde{r}_e + \frac{\alpha\gamma\tilde{r}_e^2}{2(\gamma + 2\lambda)} - \frac{\alpha^2\gamma\tilde{r}_e^3(\gamma + 4\lambda)}{4(\gamma + 2\lambda)^2} + \frac{\alpha^3\gamma\tilde{r}_e^4(\gamma^2 + 4\gamma\lambda + 8\lambda^2)}{8(\gamma + 2\lambda)^3} + \cdots. \tag{8}$$

Therefore, if we insert the experimental equilibrium bond length $\tilde{r}_e$ and the other model parameters, we obtain r_e appearing in the potential (2). Note that $r_e = \tilde{r}_e$ when either $\alpha = 0$ or $\gamma = 0$ because in such cases, $V(r)$ becomes a Kratzer potential (see also Eq. 7). We may try a similar calculation for D_e, but it is not necessary to spend time in this kind of discussion because any book on spectroscopy shows that the standard procedure for the construction of a potential energy curve is to fit the theoretical spectrum to the experimental one [2].

In conclusion, we mention another weakness in the paper by Ibrahim et al. They calculated the canonical partition function as

$$Z(\beta, N_{\max}) = \sum_{n=0}^{N_{\max}} e^{-\beta E_{nl}}, \tag{9}$$

overlooking the sum over the rotation quantum number l (commonly called J by spectroscopists and other scientists) [2, 3]. Consequently, the resulting expression for Z and the thermodynamic functions derived from it are unsuitable for the treatment of a physical problem. There are many examples of suitable physical applications of statistical mechanics in most textbooks on the subject [3] (see also a recent critique of a paper on the same subject and the example therein [4]).

3 Conclusion

Ibrahim et al. [1] proposed a potential for diatomic molecules of dubious utility [2]. The parameters D_e and r_e are not the dissociation energy and the equilibrium bond length, respectively, as they argued. The figures in their paper are incomprehensible. Finally, since they did not include the rotation quantum number in the calculation of the canonical partition function, the resulting thermodynamic functions are inapplicable to a physical system.

Author contributions

FF: conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, resources, software, supervision, validation, visualization, writing–original draft, and writing–review and editing.

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