Application of the WKB Approximation in the Solution of the Schrödinger Equation

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Physical chemistry at the undergraduate level introduces, at least qualitatively, many of the quantitative tools required for a rigorous understanding of the world on an atomic and molecular level. In particular, quantum mechanics is introduced as the exact theoretical description of chemical bonding, spectroscopy, molecular interactions, and reaction dynamics at the molecular level. While the full mathematical or computational solution of realistic quantum problems is beyond the scope of most undergraduate courses in physical chemistry, the idea that the solutions of the Schrödinger equation do describe physical and chemical properties of interest should be firmly understood even at the undergraduate level. To this end, problems that successfully model simple but realistic molecular systems and can be solved computationally without great difficulty may be useful. Various undergraduate projects designed for physical and computational chemistry have been described in this *Journal*, including methods that deal with approximate solutions of various quantum mechanical problems (1–9). Authors have presented solutions for the Schrödinger equation using spreadsheets, mathematically oriented programs, and programming languages.

Here we describe a computational experiment in which the students examine the solution of Schrödinger equation for model systems based on the Wentzel–Kramers–Brillouin (WKB) approximation (10). The project can be implemented using algebraic computer programs such as Mathematica or Mathcad, or programming languages such as Fortran or C.

A full documentation for the experiment, which is implemented in Mathematica, is available online.W

Scientific Background

The binding of atoms into stable molecules is described by the lowering of the electronic energy of the system as the nuclei take up the stable geometry of the molecular structure. The evaluation of the electronic energy as a function of the interatomic distances yields a "potential energy surface" of the molecule. The simplest such surface is the potential energy $V(r)$ for a diatomic molecule as a function of the internuclear distance, r. For stable molecules, $V(r)$ will have a minimum, $-V_0$, at the equilibrium bond distance, r_e, go to zero as $r \to \infty$, and become very large as $r \to 0$ due to electron overlap and the Coulomb repulsion of the nuclei. The energies of absorption and emission of light by molecules changing their vibrational and rotational states permits the analysis of molecular geometry and manipulation of the molecules to form lasers, etc. To determine or interpret these energies, one must determine the potential energy surfaces and then set up and solve the Schrödinger equation for the quantized vibration–rotation levels.

In this problem we shall use a good approximation to determine the energy levels of a diatomic molecule given a good (but approximate) analytic form for the intermolecular potential, $V(r)$. For a diatomic molecule the rotational quantum states are given simply and exactly by quantization of the rotational angular momentum. Thus the vibration–rotation energy of the molecule is determined by solving for the eigenvalues of the Schrödinger equation for the vibrational motion of the molecule in the full potential:

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi_{n,l}}{dr^2} + \left[V(r) + V_{l,\text{rot}} \right]\psi_{n,l} = E_{n,l}\psi_{n,l} \tag{1}$$

where

$$V_{l,\text{rot}}(r) = \frac{l(l+1)\hbar^2}{2\mu r^2}, \quad l = 0, 1, 2, \dots$$

is the rotational energy, r is the internuclear separation, and μ is the reduced mass, $m_1 m_2/(m_1 + m_2)$, of the molecule.

Although there are several ways to approach the numerical solution of the Schrödinger equation, particularly for a simple single-variable (r) system such as this, we will look at the WKB method of finding the approximate eigenvalues. This approach, which is quite accurate and conceptually simple, is based on the Bohr theory of quantization of action. The Bohr theory postulates that for stable quantum states, the periodic motion must have quantized "action", defined as the integral of the momentum over the orbit. In the case of vibrational motion bounded on the left and right by r_ℓ and r_r where $V(r_\ell) = V(r_r) = E$, the action is defined by the integral

$$I(E) = \frac{1}{\pi\hbar} \int_{r_\ell}^{r_r} \left\{ 2\mu[E - V(r)] \right\}^{1/2} dr \tag{2}$$

The WKB approximation states that the quantized levels are determined by those energies for which

$$I(E_n) = n + \tfrac{1}{2}, \quad n = 0, 1, 2, \dots \tag{3}$$

This problem seems quite simple; merely evaluate the integral for a set of E's and then interpolate to find the values at which $I(E)$ has the appropriate quantized value. However, to solve this problem on a computer involves several elementary but useful procedures of numerical analysis: choosing an efficient set of values of E for which to determine $I(E)$; finding roots $r_\ell(E)$ and $r_r(E)$ of the equations $V(r) = E$; evaluating the above integral numerically; and finally interpolating between the values of $I(E)$ to determine the values E_n at which the quantum condition is satisfied. In addition the realistic anharmonic behavior of the vibrational levels and the

variation with angular momentum can be observed, yielding, if desired, the spectroscopic constants for the trial molecule.

Application for Simple Potential Functions

The interatomic potential, $V(r)$, can be determined by electronic structure calculations or by choosing a functional form and determining the potential parameters that best fit the experimental data. A commonly used functional form is the Morse potential:

$$V_{\text{Morse}}(r) = D_e[e^{-2\alpha(r-r_e)} - 2e^{-\alpha(r-r_e)}] \tag{4}$$

where D_e, is known as the dissociation energy, α is related to the force constant, and r_e is the equilibrium internuclear separation. The Schrödinger equation has an analytical solution for the Morse potential when the rotational angular momentum term is zero. The energy levels of bound states are given analytically according to Landau and Lifshitz (*11*) by

$$E_n = -D_e\left[1 - \frac{\alpha\hbar}{\sqrt{2\mu D_e}}\left(n + \frac{1}{2}\right)\right]^2 \tag{5}$$

where $n = 0, 1, \ldots, n_{\max}$, and $n_{\max}$ is the greatest value of n for which

$$\frac{\sqrt{2\mu D_e}}{\alpha\hbar} > n + \frac{1}{2}$$

With the arbitrarily chosen $\hbar = \mu = 1$, $D_e = 200$, and $\alpha = 2$, there are *exactly* 10 bound states. Thus, the availability of the analytical result provides an opportunity to test the numerical approach.

The WKB approximation can be applied to calculate rotational energy levels of a diatomic oscillator according to eq 1. To compare this result with the results obtained in the case of the Morse potential, other common potentials of a diatomic oscillator can be used, such as the Lennard-Jones

$$V_{\text{LJ}}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]$$

and exponential-6

$$V_{\text{E6}}(r) = De^{-\alpha(r-r_0)} - 4\varepsilon\left(\frac{\sigma}{r}\right)^6$$

potentials. One can find that the accuracy of the WKB results depends on the number and distribution of energy guesses. Thus the method provides means for addressing the problems of precision and convergence in the calculations.

In the implementation of such projects for computational chemistry courses, students can be encouraged to use Fortran or C programming. Numerical techniques for finding roots, integration, and interpolation are readily available. "Numerical recipes" (*12*) and companion textbooks are an excellent source of these methods.

ᵂSupplemental Material

An expanded version of this article that includes graphical and tabular results is available in this issue of *JCE Online*.

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