CHAPTER I

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1. Introduction:

The micro-world of atoms and molecules is most aptly described by quantum mechanics. The cornerstone of quantum mechanics is the Schrödinger equation, for, its solutions, the so-called eigen-functions and eigen values hold the essence of the micro-world that they seek to describe. So, it is the end and aim of all the quantum mechanical applications to find out eigen-functions and eigen values in any given problem.

As far as the diatomic molecule is concerned the Schrödinger wave equation forms the very core of the molecular phenomena. Molecular structure reveals itself, so to say, in the spectra of the molecules; the spectra, in turn, are the results of a set of transitions between rotational levels associated with vibrational levels of a pair of electronic states. These transitions are governed by certain selection rules, which can most appropriately be derived on the basis of quantum mechanics. The intensities of spectral lines, which form another important aspect of spectra,
are governed by transition probabilities. These transition probabilities are computed with the use of eigenfunctions. Theoretical study of molecular structure of diatomic molecules thus boils down to the study of the appropriate Schrödinger equation.

One of the most important parameters that enter the Schrödinger wave equation for a diatomic molecule is the potential. Numerous potential energy functions have been proposed by investigators in this field, but unfortunately no single potential function is found to be of universal application. Only for a very few potential functions like Morse function\textsuperscript{19} and Tietz function\textsuperscript{20} is Schrödinger equation solvable exactly. But then these particular potential functions may not be suitable for all diatomic molecules. Hence attempts are being constantly made to solve the Schrödinger equation using other potential functions, though only approximately. Several approximation methods to achieve this end are available in the literature, the most well-known being the Wentzel-Kramers-Brillouin (WKB) method, and the most celebrated use of this approximation method is made in obtaining RKR (Rydberg\textsuperscript{1}Klein\textsuperscript{2}Rees\textsuperscript{3}) wave functions.
To obtain wave functions, in the RKR procedure, potential energy curves are constructed for the molecular states involved in the transition under consideration. These curves are constructed from experimental data on the molecules. Then these potential energy curves are read at any internuclear distance desired, and the Schrödinger equation solved by WKB approximation.

As is to be expected, the wave functions obtained in this manner do yield good results. In other words, the Franck-Condon factors, which are quantities proportional to transition probabilities, and other parameters thereof are indeed realistic, as experimental data have been processed in the RKR procedure. But this procedure is long and laborious even if one uses a computer; secondly, since potential values have to be read from the graph of potential energy curves, there is bound to be some error involved. This method of obtaining the potential values would certainly be not as accurate as an analytical expression for potential would yield. (Only recently Huffaker^{4} (1977) has developed analytic expressions for RKR potentials.) Hence other approximation methods which are
capable of handling analytical potential functions are often resorted to in molecular problems.

The RKR results are expected to be realistic as stated earlier, but the validity or otherwise of computational results is really to be seen in the comparison of the theoretical results with the corresponding experimental ones; for instance, the computed Franck-Condon factors are to be compared with the observed band-strengths. If there is agreement between the theoretical and experimental sets it is well and good; but such agreement may not often be observed. In such circumstances one has to examine critically both the theoretical methods and experimental findings. In the light of theoretical computations such as transition probabilities, one contrives better and better experimental results; on the other hand, to achieve better agreement with experimental results, theoreticians propose better and better theoretical models and try to refine the theoretical tools. Refinement in one aspect is complementary to refinement in the other and a kind of 'competition' between the two goes on. Thus, possession of both the experimental data and theoretical predictions is of paramount importance in the study of molecular structure.
In view of the foregoing remarks, in the present investigation, different theoretical methods of computation of transition probabilities have been examined with respect to three diatomic molecules. Three potential functions have been tried and tested as to their suitability in obtaining accurate transition probabilities for these chosen molecules. Wherever experimental data on intensities of bands are available, use has been made of them to compare the band strengths with theoretically computed Franck-Condon factors; also, these experimental band intensity data have been processed to derive another important parameter about the molecule, viz., variation of electronic transition moment with internuclear distance. Broad outlines of all these aspects of the present investigation have been described in the following section.

2. The Problem:

In the light of the foregoing, it is of great importance to solve the Schrödinger equation and obtain vibrational wave functions. For the potential entering the Schrödinger equation for a diatomic molecule, a large number of potential functions have been proposed. But not all of them are acceptable potential functions.
There are a few general criteria that a potential function should satisfy in order that it can be called a good potential function. These criteria may be briefly stated as follow:

(a) The potential function should asymptotically tend to a finite value as the internuclear distance $r$ tends to infinity.

(b) The potential energy curve should have a minimum at $r = r_e$, the equilibrium internuclear distance.

(c) As $r \to \infty$, the value of the potential energy should tend to infinity.

If $U(r)$ denotes potential energy, one could write the first two criteria stated above as:

(a) $U(r_e) - U(\infty) = -D_e$

where $D_e$ is the dissociation energy of the molecule.

(b) $\left( \frac{dU}{dr} \right)_{r = r_e} = 0$.

Now, most of the potential functions proposed do not satisfy the criterion (c) but satisfy the first
two. Such potential functions give the conventional form of the potential energy curve with a deep minimum. But as to which potential function suits a given molecule has to be decided only on the basis of comparison of the potential energy curve that the potential function seeks to describe, with the true potential energy curve plotted from experimentally determined parameters like $r_e$, $w_x$, $k_e$ etc. Comparative tests on these lines for some of the potential functions on a few diatomic molecules have been made by Lotmer, Coolidge, James and others. A thorough review of the potential energy functions has been made by Varshni (1957). But in all these studies of potential energy functions the emphasis has been on the direct study of potential functions and their performance with regard to the yielding of molecular parameters like $\alpha_e$, $w_e x_e$ etc. But in our present investigation the emphasis is not so much on the direct performance of the potential function as on the vibrational wave functions derived by using the potential function. So we test a given potential function by posing for ourselves the following questions and by trying to answer them: With the given potential function, is the Schrödinger equation solvable exactly? If not, how best to solve the Schrödinger equation approximately?
Once the Schrödinger equation is solved, exactly or approximately, the next question is: how good are the wave functions so obtained? To answer this question we compute what are known as Franck-Condon factors which are quantities proportional to transition probabilities. The overlap integral
\[ \int \psi_{v'}^* \psi_v \, dr \]
is computed using the vibrational wave functions \( \psi \)'s and the square of this integral forms the Franck-Condon factor (FCF) for the transition \((v',v'')\). These theoretically predicted quantities are comparable with the experimentally determined band strengths. If reliance is placed on experimental observations, a comparison of the theoretically predicted Franck-Condon factors with the corresponding band strengths indicates as to how 'good' the computed Franck-Condon factors are, and therefore, in turn, how good the potential functions are. But then the computed wave functions depend not only on the potential function, but also on the approximation method employed to derive the wave functions. Only if the Schrödinger equation is solvable exactly for a particular potential function, the wave functions depend only on the potential function; but, as pointed out earlier, only for a few potential functions is Schrödinger equation solvable exactly. Hence, we can say, in a general way, that the accuracy
or otherwise of the wave functions depends on two factors: (i) the potential function and (ii) the method employed to solve the Schrödinger equation.

Even when the Schrödinger equation is solvable exactly, one is not sure that the potential function used in the Schrödinger equation is suited to the particular electronic state of the molecule under study. In other words, one is not sure that 'exact' wave functions truly describe the molecular state under investigation. In such circumstances, the problem should be solved in a realistic way, in the sense that experimental data should be used to obtain realistic potential values and these, in turn, used to solve the Schrödinger equation by some 'good' approximation method. Then the solutions so obtained may be termed as realistic solutions.

With the foregoing in view it was contemplated by the present investigators that the problem should be tackled in the following manner. We should be in possession of 'realistic' solutions of the Schrödinger equation; at the same time, different approximation methods which could handle any analytic potential function should be employed to solve the Schrödinger equation.
Then one could compare the realistic solutions with the different sets of solutions obtained on the various approximation methods. Such a comparison would tell us how good the approximate solutions are when compared with the realistic solutions. Using a particular potential function but several approximation methods of solving the Schrödinger equation different sets of solutions could be obtained. Then a comparison of these solutions with the realistic solutions would give a comparative picture of the different approximation methods employed. If, on the other hand, one uses different potential functions and gets the solutions by employing only one approximation method, a comparison of the approximate wave functions or of quantities derived from them with the corresponding realistic quantities would throw light on the suitability of the particular potential function for the problem on hand.

It is now an established fact that the RKR or RKRν procedure coupled with potential energy curve constructed on empirical data yields 'true' or 'realistic' wave functions. This is as it should be, for, the potential energy curve constructed by making use of experimental data must truly represent the
electronic state of a molecule. Therefore, when one uses such realistic potentials one has reasons to hope for good results. Also, the WKB method is a well-known good approximation method. As this method is employed along with the realistic potentials for computing wave functions one can take RKR wave functions as representing true wave functions. Hence, the real test of an approximation method or of a potential function is provided by a comparison of the wave functions computed by using the particular approximation method or by using the particular potential function, with the RKR wave functions.

In the light of these observations we have chosen three diatomic molecules, two approximation methods and three different analytic potential functions for the present investigation.

The two approximation methods chosen are: (i) Langer's method\textsuperscript{10} and (ii) method of iteration due to Herman et al.\textsuperscript{11} These two methods have been chosen because of the following two reasons: (a) firstly, both the methods are simple to handle and (b) it is possible to process any analytically expressible potential function by these two methods.
The molecular transitions chosen are: (i) CN (B → A)\textsuperscript{12}, (ii) SnO (D → X)\textsuperscript{13,14}, (iii) PbO (B → X)\textsuperscript{15}. The B → A transition of CN has been recently observed experimentally and the vibrational intensities of the bands of this transition have been very recently measured accurately (Gorbal 1977)\textsuperscript{16}. Only Morse Franck-Condon factors of the bands were available in literature\textsuperscript{17}. Hence it was felt that there was ample scope for work on this particular transition.

The other two molecules chosen are heavy compared to CN. Choosing these heavier molecules enables one to find out if the mass of the molecule affects the results found by the approximation methods. Also, not much theoretical work on these two molecular transitions exists in literature — only Morse potential results of Franck-Condon factors are available\textsuperscript{13,14,15}; however, experimental intensities of the bands of these transitions are available. These could be processed and compared with the theoretically predicted transition probabilities.

The potential functions chosen are Rydberg\textsuperscript{18} potential function, and two of six potential functions
proposed by Varshni (1957). The reasons for our selecting these potential functions stem from the analysis of Varshni of the performance of the various potential functions. Varshni makes use of the Sutherland parameter $\Delta = \frac{K_{e} r_{e}}{2D_{e}}$ and two functions $F$ and $G$ defined as

$$F = - \frac{X_{r_{e}}}{3} + 1 = \frac{\alpha_{e} w_{e}}{6B_{e}^{2}}$$

$$G = - \left[ \frac{5}{3} X^{2} - Y \right] r_{e}^{2}$$

$$w_{e} x_{e} r_{e}^{2} x 64 \pi^{2} c x 1.6597 x 10^{-24} \mu_{A}^{2}$$

$$= \frac{1}{h}$$

$$X = U''(r_{e})/U''(r_{e}), \quad Y = U^{iv}(r_{e})/U''(r_{e})$$

where $U$ is potential energy and primes indicate derivatives w.r.t. $r_{e}$.

to test the performance of the potential functions. Varshni concludes that the Rydberg potential is distinctly better than the Morse function. On the basis of 23 diatomic molecules for which experimental parameters
like $\alpha, \beta, \gamma, \delta$ etc. existed, Varshni prepared a list of potential functions for which the accuracy increased in the following order:

(i) Morse, Pöschl-Teller, Rosen - Morse, Frost-Musulin
(ii) Rydberg (iii) Third, sixth (of the potential functions proposed by him). However, the third potential function was not chosen as the expression for this potential involves $r$ in the denominator and with this, it is impossible to process the function in Langer's method. Hence we have chosen the first potential function instead of the third. The sixth potential function has also been processed. Thus, in all, we have chosen three potential functions, viz., (i) Rydberg potential function, (ii) Varshni's first potential function and (iii) Varshni's sixth potential function.

The details of processing these functions in the two methods, viz., Langer's\textsuperscript{10} and iteration\textsuperscript{11} and the RKR procedure are set forth in the next chapter.
References

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7. Coolidge, James, and Vernon, Phys. Rev. 54, 726 (1938).


