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Model for vibrations associated with molecular Rydberg transitions

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A model consisting of a proton which is harmonically bound along a line and an electron bound to the proton is treated. Spectral features of the model system considered include energy level shifts, vibronic intensities, and interactions between members of degenerate manifolds not predicted by the application of the Born–Oppenheimer approximation to the model system. A time dependent process resulting in vibrationally induced preionization is also investigated. The results have special physical relevance in that they serve to facilitate understanding of vibrational effects on molecular Rydberg spectra.

Keywords: Vibrational effects upon Rydberg spectra—Perturbation theory approach for a model system.

1. Introduction

The harmonic oscillator and the hydrogen atom eigenvalue problems were among the first successfully treated by quantum mechanics. In this research, a system is studied which has features of both. The system consists of an electron associated with a proton which is itself harmonically bound.

The applicability of the Born–Oppenheimer approximation to molecules relies upon the frequencies of molecular vibrations being much less than the frequencies of electronic transitions. However, for any particular vibrational manifold in a molecule, there exists a spectral region in which the vibrational frequency is nearly identical to a particular electronic frequency. In such a spectral region, the Born–Oppenheimer approximation is no longer appropritate. In fact, as one

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moves through this degenerate region into the spectral region in which the vibrational frequency is greater than the electronic frequency, one might think of applying what could be called the *anti*-Born–Oppenheimer approximation in order to obtain agreement between calculated and observed features [1]. In this last spectral regime time-dependent effects such as vibrationally induced preionization may occur. For the calculations in this paper, neither the Born–Oppenheimer approximation nor its opposite is featured; rather a particular perturbative approach is used which favors neither regime and which is exact order by order.

2. Model system

The model system (Fig. 1) consists of a proton constrained to motion along a line where it is subject to a Hooke's law potential and an electron attracted to the proton by a coulombic potential (three-dimensional). The equilibrium position of the proton is the origin of an imposed coordinate frame. This model yields a Rydberg-type spectrum with associated vibrational features.

The Hamiltonian operator, in atomic units (a.u.) is

$$H=-\tfrac{1}{2}\nabla^2(\rho,\theta,\phi)-\frac{1}{2m}\frac{\partial^2}{\partial\delta^2}+\tfrac{1}{2}\kappa\delta^2-\frac{1}{\eta}$$

where ρ, θ, and ϕ are spherical polar coordinates for the position of the electron with respect to the origin; η is the distance between the electron and the proton; δ is the displacement of the proton from its equilibrium position as measured along the Z axis; m and κ are the rest mass and force constant of the oscillator, respectively.

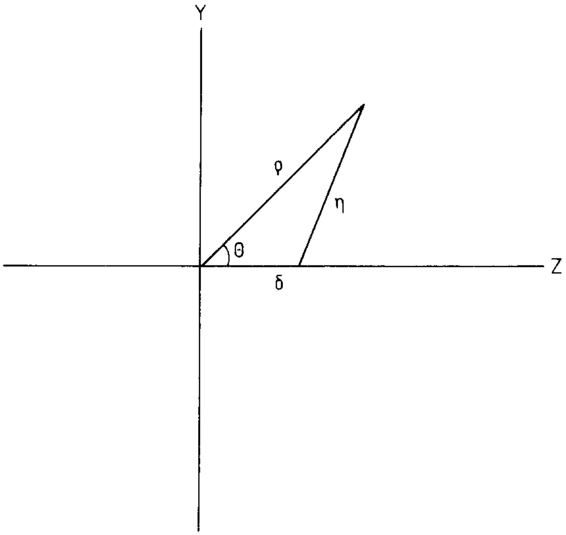

Fig. 1. Model system

3. Basic theory

In order to obtain the spectrum of the model system through the use of Rayleigh–Schrödinger perturbation theory, the quantity $1/\eta$ is expressed as a function of ρ, θ, and ϕ. This leads to two series, each of which is valid over a unique region depending upon the relation between ρ and δ.

$$\text{series } f_1\text{: } \frac{1}{\eta}=\frac{1}{\mu\delta}\sum_{s=0}^{s=\infty}\frac{\rho^S}{(\mu\delta)^s}P_s(\cos\theta);\ \rho<\delta$$

$$\text{series } f_2\text{: } \frac{1}{\eta}=\frac{1}{\rho}\sum_{s=0}^{s=\infty}\frac{(\mu\delta)^s}{\rho^s}P_s\,(\cos\theta);\ \rho>\delta.$$

Mu (μ) in a dimensionless parameter which keeps track of the power of δ throughout the perturbation calculations. Using the Heaviside function $\Theta(\rho-\delta)$ and defining

$$\Theta_1=1-\Theta(\rho-\delta)$$

the Hamiltonian operator may be formally expressed as

$$\begin{aligned} H &= -\tfrac{1}{2}\nabla^2(\rho,\theta,\phi)-\frac{1}{2m}\frac{\partial^2}{\partial\delta^2}+\tfrac{1}{2}\kappa\delta^2-\frac{1}{\rho}+\lambda\left[\Theta_1(f_2-f_1)+\frac{1}{\rho}-f_2\right]\\ &= H^0+\lambda V \end{aligned} \tag{1}$$

Here, λ is another dimensionless parameter which is used to keep track of the order of the perturbation in the same sense as the usual developmental parameter. As it turns out, more than one power of λ may be needed to get all terms corresponding to a single power of μ. The point of view which emerges is that organizing the results according to powers of μ makes the most sense.

The Hamiltonian operator (1) is now seen to be composed of a part which is simple and a part which is small. The simple part is a sum of the well-characterized hydrogenic and harmonic oscillator Hamiltonians (each referred to a common origin), while the small part consists of a mixture of terms which will be called the perturbation. Notice that the term $1/\rho$ in the perturbation is restricted to a comparatively small domain ($\rho<\delta$).

For the unperturbed part of (1) we have independent systems. The zero-order wave functions are a product of the hydrogenic and harmonic oscillator eigenfunctions. They are functions of ρ, Θ, ϕ, and δ. The higher order wave functions and energies follow the standard Rayleigh–Schrödinger perturbation theory formulations in which the hydrogenic continuum eigenfunctions [2] have been included.

4. Static case calculation

In order to explore the methodlogy of using first order perturbation theory as involving both the bound and continuum state wave functions of the hydrogen atom and the two developmental parameters, the following test problem is treated [3].

Consider a proton located on the Z axis a distance δ from the origin of a set of coordinate axes. Let there be an electron attracted to the proton by a coulombic potential (this is our model without the inclusion of the proton dynamics). The electric moment of this system in the ground electronic state ($[n, l, m] = [1, 0, 0]$) will be calculated with respect to the origin of the coordinate axes. Since the electron charge density in the ground state would be spherically symmetric about the proton, the electric moment of the system should be zero with respect to the origin.

The Hamiltonian operator for this static system is:

$$H_s = -\tfrac{1}{2}\nabla^2(\rho, \theta, \phi) - \frac{1}{\rho} + \lambda\left\{\theta_1(f_2 - f_1) + \left(\frac{1}{\rho} - f_2\right)\right\}.$$

The zero-order wave functions are $\psi^{(0)}_{n,l,m}(\rho, \theta, \phi)$ and $\psi^{(0)}_{k,l,m}(\rho, \theta, \phi)$. These are the bound and continuum state hydrogenic wavefunctions, respectively.

For the model, the electric moment operator is:

$$\boldsymbol{P}_{\text{system}} = \mu\delta\boldsymbol{k} - [\rho\cos\theta\cos\phi\boldsymbol{i} + \rho\sin\theta\sin\phi\boldsymbol{j} + \rho\cos\theta\boldsymbol{k}].$$

We wish to calculate the average value of the electric moment for the system. Because δ is constant, the proton's contribution to $\langle\boldsymbol{P}_{\text{system}}\rangle$ is $\mu\delta$. The electron's contribution to $\langle\boldsymbol{P}_{\text{system}}\rangle$ correct through the first order in μ results from consideration of the first order (λ) electronic function, $\bar{\Psi}_{1,0,0}(\rho, \theta, \phi)$. In particular,

$$\langle\boldsymbol{P}_{\text{electron}}\rangle = \int_{d\tau} \Psi^*_{1,0,0}(\rho, \theta, \phi)\boldsymbol{P}_{\text{electron}}\Psi_{1,0,0}(\rho, \theta, \phi).$$

To the first order in μ, the only non-zero terms in this expression result from the Z component of $\boldsymbol{P}_{\text{electron}}$. Evaluation of this quantity leads to [4]:

$$\begin{aligned}\langle\boldsymbol{P}_{\text{electron}}\rangle_Z = {} & -\lambda\mu\delta\tfrac{2^8}{3}\sum_{n=2}^{\infty}\frac{n^5}{(n^2-1)^4}\left(\frac{n-1}{n+1}\right)^{2n} \\ & -\lambda\mu\delta\tfrac{2^8}{3}\int_{k=0}^{k=\infty}\frac{k}{(1-e^{-2\pi/k})(1+k^2)^4}\left(\frac{1+ik}{1-ik}\right)^{2i/k} dk \\ = {} & -0.565004\lambda\mu\delta - 0.434995\lambda\mu\delta \\ = {} & -0.999999\lambda\mu\delta\end{aligned}$$

Thus,

$$\langle\boldsymbol{P}_{\text{system}}\rangle = \mu\delta - 0.999999\lambda\mu\delta.$$

The exact value of zero should have resulted since for sufficiently small δ, only the term which is linear in δ has appreciable magnitude. The small deviation of the calculated value from zero is a measure of the accuracy possible with the numerical methods employed.

As mentioned earlier, λ is used in the same sense as the usual developmental parameter of perturbation theory and as such keeps track of the type of perturbation theory formula used in the calculation. If the electric moment of this static model had been calculated through the first non-vanishing order of λ, without consideration of μ as well, then a spurious electric moment would have been obtained. That the electric moment essentially vanishes in the present calculation means that the first order (λ) wave function for the electron correctly follows the proton. This same result would have been obtained automatically by a Born–Oppenheimer calculation but as we shall see, the Born–Oppenheimer results are not quite correct when the dynamics of the nuclear motion are incorporated.

5. Parameterization of the model system

In the static case calculation where there was no quantum mechanical motion of the proton, it was possible to obtain an analytical expression for the electric moment. In general, it is not possible to obtain such analytical expressions. To proceed numerically we must choose values for the constants m and κ.

It is not unrealistic to think of vibrational amplitude in diatomic molecules as about one-fifth of the radius of the first Bohr orbit of the hydrogen atom. In the model, setting the average displacement of the proton from the equilibrium position to be $\frac{1}{5}$ a.u. leads to a value of $\beta=(m\kappa)^{1/2}=\frac{25}{2}$. This will be our choice for β.

For computational simplicity in later calculations, it is desired to have the vibrational energy increment in the model equal to the energy difference between two low-energy electronic states. For our calculations we choose this energy increment to be that between the $n=3$ and $n=4$ electronic levels of the hydrogen atom. This leads to $\kappa=0.303819$ a.u. and $m=514.285$ a.u. The mass obtained for the proton is significantly lower than the actual mass which makes it unwise to give the various quantitative results which we shall be obtaining too literal an interpretation. In fact, as we vary the parameters in this model to increase the mass of the "proton", the magnitude of the non-Born–Oppenheimer effect diminishes (as expected).

6. Ground state energy I

The ground state energy of the model system will now be calculated though the lowest non-vanishing order of the developmental parameter μ. In atomic units, the zero-order wave function for the ground state of the model is:

$$\Psi^{(0)}_{n,l,m;v}(\rho,\theta,\phi;\delta)=\Psi^{(0)}_{1,0,0;0}(\rho,\theta,\phi;\delta)=\frac{e^{-\rho}}{\sqrt{\pi}}\left(\frac{\beta}{\pi}\right)^{1/4}e^{-\beta\delta^2/2}$$

The zero-order energy for the ground state is:

$$E^{(0)}_{1,0,0;0}=-\frac{1}{2}+\frac{1}{2}\left(\frac{\kappa}{m}\right)^{1/2}$$

Let the bound state functions $\Psi^{(0)}_{n,l,m;v}(\rho,\theta,\phi;\delta)$ be represented by the ordered set of characters $(n, l, m; v)$ and the continuum state functions $\Psi^{(0)}_{k,l,m;v}(\rho,\theta,\phi;\delta)$

be represented by the ordered set of characters $(k, l, m; v)$, where it is understood that when reference is made to a particular state, n is always expressed as an integer and k is always expressed as a non-integer. The first-order (λ) energy correction to the ground state is:

$$E^{(1)}_{1,0,0;0} = \int_{\delta=-\infty}^{\delta=\infty} \langle (1,0,0;0)|\lambda\left[\theta_1(f_2-f_1)+\frac{1}{\rho}-f_2\right]|(1,0,0;0)\rangle \, d\delta.$$

Evaluating this expression and retaining only the terms of lowest order in μ yields:

$$E^{(1)}_{1,0,0;0} = \frac{\lambda\mu^2}{3\beta} = 0.0266666\cdots\lambda\mu^2 \text{ a.u.}$$

The zero-order energy of the ground state is -0.4878472 a.u. The first-order energy correction evaluated here is quite large in comparison to the zero-order energy – in fact, too large. The problem is that not all terms of order μ^2 have been included. There are terms of order $\lambda^2\mu^2$ resulting from the λ^2 perturbation theory formula which must be included. Once again, it is μ and not λ which acts as the true developmental parameter.

In the second-order (λ) energy formula, zero-order functions which interact with $(1,0,0;0)$ over the perturbation to yield energy corrections of order $\lambda^2\mu^2$ are those of the type $(n,1,0;1)$ and $(k,1,0;1)$. Evaluating this second-order energy contribution and retaining only the $\lambda^2\mu^2$ terms (these are the terms of lowest order in both λ and μ) yields:

$$\begin{aligned} E^{(2)}_{1,0,0;0} &= \frac{-\lambda\mu^2 3(2^8)}{\beta}\left\{\sum_{n=2}^{\infty}\frac{n}{(n^2-1)(151n^2-144)}\left(\frac{n-1}{n+1}\right)^{2n}\right. \\ &\quad \left. + \int_{k=0}^{k=\infty}\frac{k}{(1+k^2)(1-e^{-2\pi/k})(144k^2+151)}\left(\frac{1+ik}{1-ik}\right)^{2i/k} dk\right\} \\ &= -0.02635229\lambda^2\mu^2 \text{ a.u.} \end{aligned}$$

Combining these energy values, the correction to the zero-order ground state energy of the model system correct through the first non-vanishing order (the second order) of the developmental parameter μ is:

$$E^{(1)}_{1,0,0;0} + E^{(2)}_{1,0,0;0} = 0.00031438 \text{ a.u.}$$

In this model, a vibrational quantum is 0.024306 a.u., so that this correction to the ground state energy represents 2.6% of the zero-point energy of the system – no small amount when one is calculating rates of chemical reactions. Further, it is our zero-order energy which would be found by the Born–Oppenheimer approximation.

The Hamiltonian for the system is (1). The Born–Oppenheimer wave functions which are solutions to the Schrödinger equation resemble the zero-order wave functions in the perturbation theory calculation but are, in fact, quite different. The zero-order perturbation theory electronic wave functions are functions of ρ, θ, and ϕ and have as their reference point the origin of the coordinate axes.

Table 1. Second order vibronic energy corrections

Vibronic state	Energy to order 0 (a.u.)	Order 2 energy (a.u.)	% of vibrational interval
(1, 0, 0; 0)	−0.5000000	0.000314376	1.29%
(1, 0, 0; 1)	−0.4635417	0.00072250	2.97%
(2, 0, 0; 0)	−0.1128472	0.000061416	0.25%
(2, 1, 0; 0)	−0.1128472	0.000804779	3.31%
(2, 0, 0; 1)	−0.0885417	0.000046126	0.19%
(3, 0, 0; 0)	−0.04340278	0.0000291207	0.12%
(3, 2, 0; 0)	−0.04340278	−0.0003997801	1.64%

The Born–Oppenheimer electronic wave functions are functions of η and what might be called θ' and ϕ' which have as their reference point the center of mass of the dynamical proton. We want to solve:

$$H\psi_{\text{Total}} = E_{\text{Total}}\psi_{\text{Total}}.$$

First solve the electronic equation:

$$(-\tfrac{1}{2}\nabla^2(\eta, \theta', \phi'))\psi(\eta, \theta', \phi') = V(\sigma)\psi(\eta, \theta', \phi').$$

This yields:

$$V(\delta) = -\frac{1}{2n^2} + \tfrac{1}{2}\kappa\delta^2$$

Then solve the nuclear equation:

$$\left(-\frac{1}{2m}\frac{\partial^2}{\partial\delta^2} + V(\delta)\right)\psi(\delta) = E_{\text{Total}}\psi(\sigma)$$

It follows directly that

$$E_{\text{Total}} = -\frac{1}{2n^2} + (v + \tfrac{1}{2})\left(\frac{K}{m}\right)^{1/2}.$$

Though these Born–Oppenheimer functions have a different explicit functional dependence than the zero-order perturbation theory functions, they yield the zero-order perturbation theory energies.

The Appendix shows an alternative method for evaluating the ground state energy of the model. Energy corrections to other levels may also be calculated [5]. Table 1 lists these results.

7. Born–Oppenheimer approximation applied to the calculation of the spectrum of the model system

As a point of reference for further perturbation theory calculations, the allowed spectrum of the model system is now investigated via the Born–Oppenheimer approximation. Only the Z component is considered here, bringing in the electric moment operator $\mu_Z = \delta - \rho \cos \theta \equiv \delta - Z$.

The calculation is performed in two parts. First, the transition moment is determined as a function of δ,

$$\mu_{1,i}(\delta) = \langle \psi_{1,0,0}(\eta, \theta', \phi') | \delta - Z | \psi_{i,l,m}(\eta, \theta', \phi') \rangle.$$

The quantity $(Z-\delta)$ is the Z coordinate of the electron, $\eta \cos \theta'$. The transition moment will be non-zero only for the states $(k, 1, m)$ and $(n, 1, m)$, $n > 1$. When the integrations over the coordinates of the electron are performed, $\mu_{1,i}(\delta)$ becomes independent of δ.

Second, the nuclear contribution to the transition moment is considered:

$$\mu'_{0,v} = \int_{d\delta} \psi_0(\delta) \mu_{1,i}(\delta) \psi_v(\delta).$$

Since $\mu_{1,i}(\sigma)$ is independent of δ, $v = 0$ due to the orthogonality of the Hermite polynomials .

Thus, at the level of the Born–Oppenheimer approximation only the $(0, 0)$ vibronic transitions occur for the system initially in the ground state. This corresponds to transitions between Born–Oppenheimer wave functions having indices $(1, 0, 0; 0)$ and $(i, 1, 0; 0)$ ($i = n$ for the bound states and $i = k$ for the continuum states). In general, at the level of the Born–Oppenheimer approximation Z-polarized vibronic transitions are symmetry allowed between states of the type $(i, l, m; v)$ and $(j, l \pm 1, m; v)$. These are (v, v) type vibronic transitions. Any other transitions having non-zero intensity represent deviations from the Born–Oppenheimer approximation results.

8. First infrared transition

The first infrared transition for the model is a transition between the states $\Psi_{1,0,0;0}$ and $\Psi_{1,0,0;1}$. This is a $(0, 1)$ type vibronic transition which is not found in the Born–Oppenheimer spectrum because the electron follows the proton exactly and the electric vector of the light has nothing with which to interact. Using perturbation theory, which does not require the electron to follow the proton, a transition dipole moment of order μ^1 may be calculated. The existence of a non-zero electric dipole moment in a molecule such as deuterium hydride is not unknown [6]. For the model, this non-zero value results from the moment due to the electron $(-0.20047199\lambda\mu)$ not quite cancelling the moment due to the proton $(\mu/5)$. Thus,

$$\mu_{1,0} = \int_{d\delta} \langle \Psi_{1,0,0;1} | (\mu\delta - \rho \cos \theta) | \Psi_{1,0,0;0} \rangle$$
$$= -\mu(0.00047199) \text{ a.u.}$$

9. Vibrational structure in Rydberg series

Upon electronic excitation, neither the force constant nor the equilibrium internuclear distance is altered. This might be called molecular Rydberg behavior of a pure kind. Any transition intensities calculated which have non-zero values and which are not due to either of these factors might be called vibrational structure of a pure Rydberg transition. (Of course, any actual structure found in molecular Rydberg series could arise from the fact that excitation of what is regarded as a non-bonding electron may in actuality be affecting the bonding. In such a situation we must also consider any changes in the force constant and the anharmonicity of the potential wells associated with each electronic state. However, this situation would not correspond to what we have defined as Rydberg behavior of a pure kind.) Within the context of the model system, transitions of the type $\Psi_{1,0,0;0}(\rho, \theta, \phi; \delta) \rightarrow \Psi_{n,l,m;1}(\rho, \theta, \phi; \delta)$ other than the first infrared transition are sought.

Considering all possible wave functions, it is found that to the lowest non-vanishing order of the developmental parameter (μ^1) the only functions which yield non-zero values for the transition dipole moment from the state $\Psi_{1,0,0;0}(\rho, \theta, \phi; \delta)$ are those of the type $\Psi_{n,0,0;1}(\rho, \theta, \phi; \delta)$ and $\Psi_{n,2,0;1}(\rho, \theta, \phi; \delta)$. Evaluation of the Z component of the moment for the particular transition $\Psi_{1,0,0;0}(\rho, \theta, \phi, \delta) \rightarrow \Psi_{2,0,0;1}(\rho, \theta, \phi; \delta)$ leads, after a lengthy calculation, to $\mu_{(1,0,0;0),(2,0,0;1)} = -\mu(0.0862298)$ a.u.

Comparison of the squares of the transition moments shows that this transition is about 1/75th as intense as the $(1, 0, 0; 0) \rightarrow (2, 1, 0; 0)$ transition which is predicted by the Born–Oppenheimer approximation. As another way of making the comparison, the intensity of the transition $\Psi_{1,0,0;0}(\rho, \theta, \phi; \delta) \rightarrow \Psi_{2,0,0;1}(\rho, \theta, \phi; \delta)$ is slightly greater than that of the hydrogen atom transition $(1, 0, 0) \rightarrow (7, 1, 0)$. Thus, this calculation shows that not only does a $(0, 1)$ type transition exist but that it has significant intensity.

Since the parameters for the model system have been chosen to yield a degeneracy in the spectrum (recall that the energy separation between $n = 3$ and $n = 4$ is a vibrational interval), it is not possible to simply calculate a moment of order μ^1 for a $(0, 1)$ type transition from the state $\Psi_{1,0,0;0}$ to the degenerate manifold using non-degenerate perturbation theory. This degenerate manifold consists of the seven zero-order members $(3, 0, 0; 1)$, $(3, 1, 0; 1)$, $(3, 2, 0; 1)$, $(4, 0, 0; 0)$, $(4, 1, 0; 0)$, $(4, 2, 0; 0)$, and $(4, 3, 0; 0)$. The intensity of any transition to this manifold will be distributed amongst the seven members. For the member $(4, 1, 0; 0)$ there exists a zero-order transition dipole moment with respect to the ground state. Since any member of the manifold may have significant amounts of this zero order member after the degeneracy is resolved, calculation of the transition moment to order μ^1 is not justified. An important aspect of this degeneracy is not the distribution of the intensity but rather the amount and pattern of the splitting.

10. Accidental degeneracy: Energy splitting of the seven-fold degenerate manifold

The energy level splitting of the seven-fold degenerate manifold is calculated to the lowest non-vanishing order of the developmental parameter μ using degenerate perturbation theory. Taking into account all possible interactions and evaluating the resulting 7×7 secular equation [7], the roots are determined to be: $E^{(1)}=0.000000$, $\pm\mu/\beta^{1/2}0.00130207$, $\pm\mu/\beta^{1/2}0.00219537$, and $\pm\mu/\beta^{1/2}0.00818181$ a.u. For $\beta=12.5$ and a vibrational quantum equal to 0.02430556, the maximum splitting of the manifold is 19% of a vibrational quantum.

In an actual molecule a seven-fold degeneracy, involving as it does the l-type degeneracy of the model system, would not be likely to occur. An accidental degeneracy between two vibronic states such as e.g. $(4,0,0;0)$ and $(3,1,0;1)$ would be more likely, but the fact that a two-fold degenerate manifold exists rather than a seven-fold degenerate manifold does not significantly diminsh the magnitude of the expected energy splitting. If the energy splitting between the states $(4,0,0;0)$ and $(3,1,0;1)$ is calculated for the model system, again a sepration of 19% of a vibrational quanta is found. Unexpected deviations from a good fit to the Rydberg formula could, according to this calculation, accidentally occur.

Only states having the magnetic quantum number m equal to zero have been considered here. The actual degenerate manifold for the model system has twenty-five members which includes states having $m=0$, $m=\pm1$, and $m=\pm2$. If these twenty-five members are considered within the context of degenerate perturbation theory, the resulting 25×25 matrix block-factors into seven distinct non-zero and non-interacting matrices, one of which contains only the members having $m=0$. None of the other blocks contain members which have $m=0$. Thus, the 7×7 $m=0$ block of the 25×25 matrix may be treated independently of the other blocks without introducing error into the calculation of the splitting of the seven-fold degenerate manifold.

11. Vibrationally induced pre-ionization

Suppose the model system is excited with light of a frequency corresponding to the energy difference between the ground state $(1,0,0;0)$ and the state $(5,1,0;0)$. The resulting electric dipole transition is clearly a transition between two bound states. If the ground state plus one vibrational quantum is thermally populated, excitation of the system by light of exactly the same frequency could also cause a transition between the states $(1,0,0;1)$ and $(5,1,0;1)$. For the model system, the state $(5,1,0;1)$ lies above the ionization limit and thus the transition $(1,0,0;1)\rightarrow(5,1,0;1)$ will be followed by a transition into the continuum. The width of the spectral line resulting from this possibility is of interest and can be calculated to the lowest non-vanishing order of the developmental parameter within the framework of the model.

A width can be obtained in various ways. Here, use is made of the fact that linewidths appear naturally in electric dipole susceptibility theory. The susceptibility χ, defined as the dipole expectation value per unit driving field, is the sum of so-called positive and negative frequency parts, χ_+ and χ_-. In terms of an orthonormal basis where N, R, and S are members of the set, N being the true ground state of the system,

$$\chi_- = \mu_{N,S} g^{-}_{S,R} \mu_{R,N}$$

and

$$\chi_+ = \mu_{N,R} g^{+}_{R,S} \mu_{S,N}.$$

The g's are the usual ω Fourier transforms of correlation functions obeying the relationships [8],

$$\omega g^{-}_{S,R} = -\int_{d\delta} \langle S|R\rangle - \left\{ i\Theta(-t) \int_{d\delta} \langle S|H|R(t)\rangle \right\}\Bigg|_{\omega}$$

and

$$\omega g^{+}_{R,S} = \int_{d\delta} \langle R|S\rangle - \left\{ i\Theta(-t) \int_{d\delta} \langle R|H|S(t)\rangle \right\}\Bigg|_{\omega}.$$

Physically, ω is the frequency of light which interacts with the system. Absence of a t following a wavefunction indicates that it is calculated at $t = 0$. For a basis in which each of the elements is a simple discrete energy eigenfunction of H with the zero of energy taken as the energy of the ground state, the g's have a particularly simple form:

$$g^{-}_{S,S} = \sum_Q \frac{1}{\omega_Q - \omega + i\gamma_Q} \quad \text{and} \quad g^{+}_{R,R} = \sum_Q \frac{1}{\omega_Q + \omega - i\gamma_Q}.$$

(The damping term, γ_Q, is gratuitously included). From these relationships, the susceptibility becomes

$$\chi = 2 \sum_Q \mu^2_{N,Q} \frac{\omega_Q}{\omega^2_Q - \omega^2 + 2i\omega\gamma_Q}$$

an expression which is often seen in formulas for the index of refraction of the Lorentz–Lorenz type. It is the quantity $2\gamma_Q$ in the denominator of the susceptibility which corresponds to the phenomenological Γ in the Lorentz–Lorenz equation. In our case the damping will arise naturally because the final state is in the continuum.

If the ground state N is not the true ground state, but rather is the true ground state plus one vibrational quantum the previous equations remain uhanged in form (provided one avoids the problem of infrared fluorescence), and γ_Q may be calculated using the general expressions for χ_- and $\omega g^{-}_{S,R}$. Even so, these equations require the wavefunction for N to be the true one.

As a sufficient approximation in what follows, the zero-order perturbed function for N is used. The basis employed is the set of functions $(n, l, m; v)$ and $(k, l, m; v)$.

Beginning with the expression for χ_-, the appropriate $g^-_{S,R}$ term is sought. The Hamiltonian for this study is, except for a shift in the zero of energy, again equation (1). To order μ^0, the electric dipole moment $\mu_{(1,0,0;1),S}$ contains contributions from two types of states for Z-polarized transitions. These states are of the type $(n, 1, 0; 1)$ and $(k, 1, 0; 1)$. This leads to four possible g^- terms. By the triangle condition and the orthogonality of the Laguerre polynomials, only two of these terms are non-zero through order $\mu^2(\lambda V = -\lambda\mu\delta \cos\theta/\rho^2)$. These terms of least order are

$$g^-_{(n,1,0;1),(n,1,0;1)} \quad \text{and} \quad g^-_{(k,1,0;1),(k,1,0;1)}.$$

The quantities $\omega_{(5,1,0;1)}$ and $2\gamma_{(5,1,0;1)}$ are the frequency and the half-width of the transition $(1, 0, 0; 1) \rightarrow (5, 1, 0; 1)$, respectively. The particular term which must be evaluated is $g^-_{(5,1,0;1),(5,1,0;1)}$ since it is the only term which contains $\omega - \omega_{(5,1,0;1)}$ in a way such that it will lead to $2\gamma_{(5,1,0;1)}$. Note that $\omega_{(1,0,0;1)} \equiv 0$. Inserting the unit dyadic $|q\rangle\langle q|$, where $|q\rangle$ includes any time independent zero-order function which interacts with $(5, 1, 0; 1)$ through the Hamiltonian, into the expression for $g^-_{(5,1,0;1),(5,1,0;1)}$, we obtain:

$$\omega g^-_{(5,1,0;1),(5,1,0;1)} = -1 - \left\{ i\theta(-t) \int_{d\delta} \langle (5,1,0;1)|H|q\rangle\langle q|(5,1,0;1)(t)\rangle \right\}\Bigg|_{\omega} .$$

Taking into consideration all interacting $|q\rangle$'s, retaining only those terms to the lowest order in μ, and disregarding all resulting terms which correspond to a shift in the frequency of the spectral line of interest, we are left with the expression:

$$g^-_{(5,1,0;1),(5,1,0;1)} = -1 \div \left\{ (\omega - \omega_{(5,1,0;1)}) - \int_{dk} \frac{\left[\int_{d\delta} \langle (5, 1, 0; 1)|\lambda V|(k, 0, 0; 0)\rangle\right]^2}{\omega - \omega_{(k,0,0;0)}} - \int_{dk} \frac{\left[\int_{d\delta} \langle (5, 1, 0; 1)|\lambda V|(k, 2, 0; 0)\rangle\right]^2}{\omega - \omega_{(k,2,0;0)}} \right\}.$$

When $\omega = \omega_{(5,1,0;1)}$ this expression has singularities for that value of k which puts the continuum state in resonance with the quasi-bound state, i.e., $\bar{k}$. What is more, the g^- has the form of a partial susceptibility so that the damping constant can be read-off directly. Then accounting for the singularities by the residue theorem we have,

$$i\gamma_{(5,1,0;1)} = i\pi \left\{ \left[\int_{d\delta} \langle (5, 1, 0; 1)|\lambda V|(k, 0, 0; 0)\rangle\right]^2 + \left[\int_{d\delta} \langle (5, 1, 0; 1)|\lambda V|(k, 2, 0; 0)\rangle\right]^2 \right\} \delta_{k,\bar{k}}.$$

Evaluation of this equation at $\bar{k} = 0.092796$ $(\omega_{(k,0,0;0)} = \omega_{(k,2,0;0)} = \omega_{(5,1,0;1)})$ yields:

$$\gamma_{(5,1,0;0)} = \lambda^2\mu^2 2.728 \times 10^{-6}\ \text{a.u.}$$

Thus,

$$\Gamma_{(5,1,0;1)} = 5.456 \times 10^{-6}\ \text{a.u.} = 1.197\ \text{cm}^{-1}.$$

A natural linewidth for a strong electronic transition is about $0.001\ \text{cm}^{-1}$ [9]. As expected, $\Gamma_{(5,1,0;1)}$ is much broader than this. At elevated temperatures, the broadened line will appear in the spectrum of the model system prior to the continuum threshold. Of course, exactly superimposed upon this broadened line will be the sharp line corresponding to the normal transition $(1,0,0;0) \rightarrow (5,1,0;0)$.

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Appendix. Ground state energy II

As a further check on the calculation of the ground state energy and as a feasibility study concerning the selection of perturbation theory basis sets for calculations concerning the model system, the ground state energy of the model system is calculated through order μ^2 with the employment of a perturbation theory basis set derived from discrete Laguerre functions rather than from Laguerre functions.

Since the discrete Laguerre functions are not eigenfunctions of $H^{(0)}$, the perturbation theory must be modified. The modified theory gives results invariant to the basis set, and hence it might be called invariant perturbation theory [10]. The Rayleigh–Schrödinger form of this theory will be used here.

The Hamiltonian operator for the model system is identical to (1).

Let $\psi_{1,0,0;0}(\rho, \theta, \phi; \delta)$ be the true ground state function for the model system. We want to solve the eigenvalue equation

$$H|\psi_{1,0,0;0}(\rho, \theta, \phi; \delta)\rangle = E_{(1,0,0;0)}|\psi_{1,0,0;0}(\rho, \theta, \phi; \delta)\rangle$$

for the true energy of the ground state, $E_{(1,0,0;0)}$. If an arbitrary basis set $|\bar{\psi}_0\rangle$, $|\bar{\psi}_1\rangle, |\bar{\psi}_2\rangle, \ldots$ is chosen such that the first member of the set is not only an approximation to $\psi_{(\rho,\theta,\phi;\delta)1,0,0;0}$ but also is normalized according to the condition $\int_{d\delta} \langle\bar{\psi}_0|\psi_{1,0,0;0}(\rho, \theta, \phi; \delta\rangle = 1$, then the true ground state function may be expanded in terms of the arbitrary basis. The expression which results for the energy of the ground state is (through order μ^2):

$$E_{(1,0,0;0)} = \int_{d\delta} \langle\bar{\psi}_0|H|\bar{\psi}_0\rangle + \sum_{i,j=1}^{\infty} \left[\int_{d\delta} \langle\bar{\psi}_0|\lambda V|\bar{\psi}_i\rangle\right] M_{ij} \left[\int_{d\delta} \langle\bar{\psi}_j|\lambda V|\bar{\psi}_0\rangle\right].$$

Here, M_{ij} is the inverse of the square matrix

$$\langle\bar{\psi}_l|(E^{(0)} - H^{(0)})|\bar{\psi}_m\rangle;\ l, m = 1, 2, 3, \ldots.$$

Let us choose as our basis set the discrete Laguerre functions $(\bar{n}, l, m; v)$:

$$(\bar{n}, l, m; v) = \bar{R}_{\bar{n},l}(\rho)\Theta_{l,m}(\theta)\Phi_m(\phi)\psi_v^{(0)}(\delta)$$

where:

$$\bar{R}_{\bar{n},l}(\rho) = 2^{3/2}\left[\frac{(\bar{n}+l+1)!}{(\bar{n}-l-1)!}\right]\frac{(2\rho)^l}{(2l+2)!}\,e^{-\rho}{}_1F_1(-\bar{n}+l+1, 2l+3, 2\rho).$$

The function $(\bar{1}, 0, 0,; 0)$ is identically the zero-order perturbation theory function and as such is an approximation to the true ground state wave function.

Evaluating the various parts of $E_{(1,0,0;0)}$ leads to

$$\int_{d\delta} \langle(\bar{1}, 0, 0; 0)|H|(\bar{1}, 0, 0; 0)\rangle = -\frac{1}{2}+\frac{1}{2}\frac{\beta}{m}+\frac{\lambda\mu^2}{3\beta}$$

$$\int_{d\delta} \langle(\bar{1}, 0, 0; 0)|\lambda V|(\bar{n}, 1, 0; 1)\rangle = -\frac{\lambda\mu}{\beta^{1/2}}\frac{\sqrt{3}}{3}\left(\frac{(\bar{n}+2)!}{(\bar{n}-2)!}\right)^{1/2}\frac{1}{(\bar{n}+1)(\bar{n}+2)}.$$

The diagonal and off-diagonal elements of M_{ij} prior to matrix inversion are [11]:

$$\int_{d\delta} \langle(\bar{n}, 1, 0; 1)|(E^{(0)}-H^{(0)})|(\bar{n}, 1, 0; 1)\rangle = -\frac{\beta}{m}-\frac{(4\bar{n}-3)}{10}$$

and

$$\int_{d\delta} \langle(\bar{n}, 1, 0; 1)|(E^{(0)}-H^{(0)})|(\bar{n}', 1, 0; 1)\rangle$$

$$= -\left[\frac{(\bar{n}-2)!\,(\bar{n}'+2)!}{(\bar{n}+2)!\,(\bar{n}'-2)!}\right]^{1/2}\left(\frac{4\bar{n}'-3}{10}\right);\ \bar{n} > \bar{n}'.$$

In the evaluationof M_{ij}, matrices ranging in size from 2×2's up to 120×120's are inverted. The value for $E_{(1,0,0;0)}$ is only slowly convergent as the size of M_{ij} is increased. Consequently, it is necessary to consider $E_{(1,0,0;0)}$ as a function of $1/N$, where N is the number of basis functions included; determine a polynomial approximation to this function; and then solve the polynomial for the value of $E_{(1,0,0;0)}$ at the limit $1/N = 0$. Following this procedure with a polynomial of order 6 gave

$$E_{(1,0,0;0)} = -0.4875327 \text{ a.u.}$$

The value calculated here using invariant perturbation theory and the discrete Laguerres differs insignificantly from the value obtained in Ground State Energy I, namely −0.4875328; however, the method followed in Ground State Energy I is the method of choice due to more rapid convergence.

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