Bender-Wu Formula, the SO(4,2) Dynamical Group, and the Zeeman Effect in Hydrogen

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and

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Asymptotic formulas are derived for the high-order perturbation coefficients for the hydrogen Zeeman Hamiltonian. The calculation of 100 coefficients in the series for the ground state are also reported. The method of calculation is based on tilting the Hamiltonian by a generator of SO(2,1) and the algebraization of the problem by means of the dynamical group SO(4,2).

Bender and Wu[1] developed a theory for the high-order terms in the Rayleigh-Schrödinger series based on its identification with negative moments of the tunneling probability.[1,2] More recently, related instanton techniques have been applied to the much harder problems of self-interacting field theories, for example to the calculation of the renormalization β function and to critical exponents.[3,4] For reasons that are not yet well understood, the zero-temperature and the high-order limit sometimes fail to commute.[5] This is the case in the hydrogen Zeeman Hamiltonian; so instanton (partition-function) techniques are not applicable even to the asymptotics of the ground state. (For related questions for the hydrogen Stark Hamiltonian, see L. Benassi *et al.*[6]

In the application of Bender-Wu theory to three-dimensional problems it has been necessary to devise special methods suitable for the particular system. Thus for the anharmonic oscillator Banks, Bender, and Wu made use of the fact that the motion transverse to the escape tubes is harmonic.[2] For the hydrogen Stark effect, Benassi *et al.*[6] used separability in parabolic coordinates. The hydrogen Zeeman Hamiltonian does not separate and we shall here employ the theory of eikonals to implement the Bender-Wu theory. This method is applicable to a large class of problems.

The spinless hydrogen Zeeman Hamiltonian is

$$H(B)=\tfrac{1}{2}\vec{p}^2-\frac{1}{|\vec{r}|}+\tfrac{1}{8}B^2(x^2+y^2)+\tfrac{1}{2}\vec{B}\cdot\vec{L}. \qquad (1)$$

(The perturbation series is known to be Borel summable.[5]) If we write

$$E(B)=\sum_{n=0}^{\infty}E_n(B^2/8)^n \qquad (2)$$

for the ground state, our first major result is

$$E_n=C_n[1+O(1/n)],$$
$$C_n=(-1)^{n+1}(4/\pi)^{5/2}(8/\pi^2)^n(2n+\tfrac{1}{2})!. \qquad (3)$$

Let us briefly sketch the derivation of (3) and its generalization to excited states. It is convenient to scale (1), so that

$$h(\lambda)=\vec{p}^2-1/|\vec{r}|-\lambda(x^2+y^2), \qquad (4)$$

with ground state $\epsilon(\lambda)=\sum_{n=0}^{\infty}a_n(-\lambda)^n$ and $E_n=2a_n/8^n$. As usual, let us denote $\Gamma(\lambda)=2\,\mathrm{Im}\,\epsilon(\lambda)$. The following dispersion relation is assumed to hold[7]:

$$a_n=(-1)^{n+1}\tfrac{1}{2\pi}\int_0^{\infty}\frac{\Gamma(\lambda)}{\lambda^{n+1}}\,d\lambda. \qquad (5)$$

Γ is related to the outgoing current at infinity which will be computed semiclassically. With $\psi(\vec{r})=\rho^{1/2}(\vec{r})\exp[i\varphi(\vec{r})]$, multidimensional WKB gives[8]

$$\Gamma=2\int_{\Omega\in\sigma}\rho(\vec{\Omega})\epsilon^{-2J(\vec{\Omega})}\nabla\varphi\cdot d\vec{s}, \qquad (6)$$

where σ is now a *small* ball around the origin and $J(\vec{\Omega})$ is the classical action from $\vec{\Omega}\in\sigma$ to the caustic. The hard part is to obtain sufficiently accurate estimates of $J(\vec{\Omega})$.

The classical equations of motion are

$$\tfrac{1}{2}\ddot{l}=l/r^3-2\lambda l,\quad l^2=x^2+y^2;\quad \tfrac{1}{2}\ddot{z}=z/r^3. \qquad (7)$$

The eikonal theory provides us with the initial conditions for trajectories starting from the surface σ. Inside σ, $\psi(\vec{r})$ is approximated by the unperturbed ground state. $\nabla\varphi$ on σ gives the initial momenta. In principle, we have to integrate equations (7) for all the trajectories starting from σ. In practice, however, we integrate the equations in a limit involving two small parameters: λ, the field strength; and α, the latitude of the point $\vec{\Omega} \in \sigma$. The smallness of λ comes from Eq. (5) and the smallness of α comes from the fact that the equatorial plane is the most probable escape path. This means that we estimate $\Gamma(\lambda)$ to the leading orders in λ. This is the origin of the $O(1/n)$ term in (3). Equations (7) can be solved by classical perturbation techniques to yield the trajectories. These are readily integrated to give the action and finally

$$J(\alpha) = \frac{\pi}{16\lambda^{1/2}} - \frac{r_0}{2} + \ln(r_0\lambda^{1/2}) + \frac{\pi}{16}\frac{\alpha^2}{\lambda^{1/2}}, \tag{8}$$

where r_0 is the radius of σ. This gives

$$\Gamma = \exp(-\pi/8\lambda^{1/2})/2^{1/2}\lambda^{3/4}, \tag{9}$$

to leading orders in λ.

The method outlined above generalizes straightforwardly to excited states.[8] Because of the degeneracy of the excited states, the situation is somewhat more complicated.

In order to verify these asymptotic results, we now describe the application of group-theoretical methods to the evaluation of 100 terms in the perturbation series for the ground state. In the application of perturbation theory difficulties arise from the continuous part of the spectrum of the unperturbed Hamiltonian. To overcome these difficulties two possible approaches may be taken. The first is to use the dynamical SO(4,2) group, which also offers a complete algebraization of the problem.[9,10] A suitable choice of the rotation angle about the T_2 generator of SO(2,1) eliminates the continuous part of the spectrum at the small price of loosing self-adjointness. Moreover, in the basis of the eigenfunctions of T_3, the resulting operator is an infinite matrix that vanishes except on the "five principal diagonals."[9] The second possibility is to use the Dalgarno-Lewis procedure in which integration over the continuous part of the spectrum is replaced by the solution of differential equations. Galindo and Pascual calculated the first five coefficients in (3) in this way.[11]

The algebraic SO(4,2) method results in a relatively simple computer implementation. Čížek and Vrscay[9] calculated the first 40 coefficients and used them for Padé summation of the series. Their calculation has now been extended to the first 100 coefficients (the full tables shall be published elsewhere). Difference-table analysis makes us confident that the coefficients we have are accurate to at least ten significant figures. The first ten coefficients are known exactly and are presented in Table I.

TABLE I. The first ten coefficients for the energy appearing in Eq. (2).

E(1) = 2

E(2) = − 53/3

E(3) = 5581/9

E(4) = − 21577397/540

E(5) = 31283298283/8100

E(6) = − 13867513160861/27000

E(7) = 5337333446078164463/59535000

E(8) = − 995860667291594211123017/50009400000

E(9) = 86629463423865975592742047423/15752961000000

E(10) = − 6127873544613551793091647103033033/3308121810000000

A fit of the coefficients E_n has been made by assuming (following Bender and Wu[1])

$$E_n = C_n[A_0 + A_1/n + A_2/n^2 + \ldots], \tag{10}$$

with C_n given in (3). The fit near $n = 50$ gives $A_0 = 1.000\,000\,098$ with A_1, A_2, and A_3 stabilized. With use of the first 69 coefficients and $A_0 = 1$, the best fit gave

$$A_1 = -2.6183, \quad A_2 = 1.283, \quad A_3 = -2.6. \tag{11}$$

Higher A_i's did not stabilize. Equation (10) with A_i in (11) is then accurate to within 0.17% for $n = 11$ and 0.000 04% for $n = 69$. As a result of this fitting procedure and the high accuracy of the coefficients thus obtained, we are confident that the asymptotic formula (3) is correct.

We have turned our attention to a recent paper by Killingbeck[12] concerning the ground-state quadratic Zeeman effect containing two very interesting results, namely a very successful calculation of upper and lower bounds for the energy using Brillouin-Wigner perturbation theory and a partitioning of the Hamiltonian which permitted him to obtain even better bounds using a one-dimensional numerical procedure. In a forthcoming paper we shall discuss the relationship of our work with that of Killingbeck in more detail; however, let us point out that the goal of the present work was simply to investigate by analytical methods the asymptotic properties and summability of the divergent Rayleigh-Schrödinger perturbation expansion because of possible implications in similar problems arising in quantum field theories rather than to obtain accurate numerical results for the energy.

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Velocity Dependence of Rotational Energy Transfer Rates in Na_2^*-Xe

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Using a technique based on the Doppler shift, we have measured the dependence of rate constants for Na_2^*-Xe rotation-changing collisions on the relative velocity. For Na_2^* in the $A^1\Sigma_u^+$ electronic state, we made measurements for four different values of the change in Na_2^* angular momentum, $\Delta = j_f - j_0$, for each of three initial j_0's. Cross sections for $j_0 = 66$ increase with velocity whereas those for $j_0 = 38$ and 16 stay constant or decrease. A dramatic decrease is observed for $j_0 = 16$ and large $|\Delta|$.

We report measurements of the velocity dependence of the rate constant k for the process

$$\mathrm{Na}_2^*(18, j_0) + \mathrm{Xe} \rightarrow \mathrm{Na}_2^*(18, j_0 + \Delta) + \mathrm{Xe} \tag{1}$$

when $\mathrm{Na}_2^*(v, j)$ is a sodium molecule in the vth vibrational and jth rotational level of the $A^1\Sigma_u^+$ electronic state. Measurements were made for $j_0 = 16$, 38, and 66, and for several values of Δ at each j_0 (we saw no evidence of perturbations[1] of line position or intensities). This inelastic process, often termed "rotational energy transfer" (RET), is dominant in most thermal-energy atom-molecule collisions, and its detailed understanding is critical for thorough understanding of other inelastic atom-molecule processes such as vibrational energy transfer and chemical reaction. The present study represents, as far as we know, the first study of the velocity dependence of any inelastic atom-molecule process in which specific rovibronic levels of the molecule were selected before the collision and analyzed afterwards.[2]

Velocity selection was achieved by use of the Doppler-shift[3,4] (VSDS) technique to select one