Bender-Wu formulas for degenerate eigenvalues

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Asymptotic formulas and large-order perturbation calculations are reported for the energy levels arising from the $3s$-$3d$ degenerate levels of hydrogen in a magnetic field.

Summability and asymptotic properties of divergent perturbation series have been of interest in quantum field theory for practical and theoretical purposes.[1-4] In nonrelativistic quantum mechanics divergent perturbation expansions have attracted attention only recently because alternative methods are often available. However, it seems reasonable to hope that a better understanding of singular perturbations in nonrelativistic quantum mechanics will contribute to the much more difficult problems in field theory. In particular, this has been the attitude of Bender and Wu,[2] who considered the asymptotics of perturbation theory for the anharmonic oscillator as a prototype (zero-dimensional) field theory. The first asymptotic analysis of perturbation expansions of relevance to atomic physics was made for the Stark hydrogen Hamiltonian[5] and subsequently for the H_2^+ molecular ion.[6]

In a recent paper[7] we have considered the Bender-Wu asymptotics for the Zeeman hydrogen Hamiltonian. We have derived the Bender-Wu formula for the ground state and the result agrees with the asymptotic behavior of the first 100 terms in the perturbation series. These terms were obtained by application of SO(4, 2) Lie algebraic techniques.[7-9]

The purpose of the present note is to announce the extension of the Bender-Wu theory to degenerate levels, in particular the $3s$-$3d$ levels of hydrogen in a magnetic field. This is the first instance of a Bender-Wu analysis when the unperturbed energy is degenerate.

The extension of the algebraic SO(4, 2) perturbation scheme to a degenerate level is somewhat involved and will be presented elsewhere.[9] In contrast, the modifications needed in the Bender-Wu theory[7,9] are slight. However, in both approaches a key element is the degeneracy lifting in the lowest order of the coupling.

The Zeeman hydrogen Hamiltonian is (in a.u.)

$$H(B)=\tfrac{1}{2}(\vec{P}-\vec{A})^2-1/|\vec{r}|,\quad \vec{A}=\tfrac{1}{2}\vec{B}\times\vec{r}. \tag{1}$$

We denote

$$E(B)=\tfrac{1}{2}Bm+\sum_{n=0}^{\infty}E_n(B^2/8)^n, \tag{2}$$

where $B=|\vec{B}|$ and m is the magnetic quantum number. The invariant subspaces of $H(B)$ have fixed L_z and parity ($\vec{B}=B\hat{z}$). In particular, for principal quantum number $n=3$ the usual ninefold degeneracy is associated with eight invariant subspaces so there are seven nondegenerate levels and one twofold degenerate level arising from the mixing of $3s$ and $3d$.

According to Bender-Wu theory[2,7]

$$a_n=(-1)^{n+1}\frac{1}{2\pi}\int_0^R\frac{\Gamma(\lambda)}{\lambda^{n+1}}\,d\lambda+O(R^{-n-1}) \tag{3}$$

and

$$\Gamma(\lambda)=\int_\sigma|\psi_0(x)|^2e^{-2S(x)}\vec{v}\cdot d\vec{\sigma}, \tag{4}$$

where σ is the surface of a large sphere in the tunneling region, $\vec{v}$ is the classical velocity on σ of the unperturbed wave function $\psi_0(x)$, and $S(x)$ is the classical action of a tunneling path starting at the point $x\in\sigma$. The details will be given in a forthcoming paper.[9] For an m-fold degenerate level the tunneling state ψ_0 in (4) corresponds to a special vector in the m-dimensional subspace of degeneracy. We choose a basis in this subspace which diagonalizes the Hamiltonian in lowest order (B^2 in the present context). This choice is unique provided the degeneracy is completely removed in the first order, as is the case for the Zeeman effect. We identify these basis vectors with the tunneling states.

For the $3s$-$3d$ level of hydrogen the tunneling states are[9]

$$\begin{aligned}\psi_{\mathrm{I}}&=-\alpha_2|3s\rangle+\alpha_1|3d\rangle,\\ \psi_{\mathrm{II}}&=\alpha_1|3s\rangle+\alpha_2|3d\rangle,\end{aligned} \tag{5}$$

where

TABLE I. Fit of the coefficients in Eq. (7) to the numerical results. The closeness of A_0 to 1 indicates agreement with the modified Bender-Wu formula. The values for A_1, A_2, A_3, and A_4 were obtained by setting $A_0=1$, and the percent accuracy corresponds to setting $A_0=1$ and taking for A_1, A_2, A_3, and A_4 the values given here.

	A_0-1	A_1	A_2	A_3	A_4	accuracy for $n=87$ (%)
I	2×10^{-7}	$-24.650\,86\pm0.000\,01$[a]	72.500 ± 0.005	2835 ± 1	$-42\,800\pm300$	0.000 23
II	3×10^{-7}	$-43.442\,76\pm0.000\,01$	798.66 ± 0.010	-9484 ± 3	$94\,300\pm500$	0.000 64

[a] The errors given are a subjective estimate of the authors based on the behavior of the extrapolation procedure.

$$\alpha_1=-\left(\frac{1}{2}+\frac{13}{(1476)^{1/2}}\right)^{1/2}\simeq-0.915\,,$$
$$\alpha_2=\left(\frac{1}{2}-\frac{13}{(1476)^{1/2}}\right)^{1/2}\simeq0.402\,. \tag{6}$$

Combining Eqs. (2) through (6) we assume the following expansion for the energy[9]

$$E_n^{\mathrm{I,II}}=(-1)^{n+1}\frac{2^{15}}{3^4\pi^{13/2}}F_{\mathrm{I,II}}\left(\frac{648}{\pi^2}\right)^n(2n+\tfrac{9}{2})!\sum_{k=0}^{\infty}\frac{A_k}{B_k(n)}, \tag{7}$$

where $A_0=1, B_0(n)=1$,

$$B_k(n)=\prod_{j=1}^{k}(2n+\tfrac{11}{2}-j)\ (k\geq1)\,,$$

and

$$F_{\mathrm{I}}=(\alpha_2+\alpha_1/2^{3/2})^2\,,$$
$$F_{\mathrm{II}}=(\alpha_1-\alpha_2/2^{3/2})^2\,.$$

We note that the ratio $E_n^{\mathrm{I}}/E_n^{\mathrm{II}}$ converges to a constant as $n\to\infty$.

We have calculated 53 terms in the expansion, Eq. (2), for each series. Each coefficient is accurate to at least thirteen significant digits and the scheme of calculation employed extends the technique developed for nondegenerate states[7-9] to degenerate states.[9] We recall that in the SO(4, 2) algebraic approach the eigenvalue problem that arises is complicated by the fact that the eigenvalue multiplies an operator which is not the identity. These results were checked by Moats and Silverstone who calculated the energy coefficients to 87th order by a related but different method and obtained agreement to 13 significant figures.[10]

To compare the Bender-Wu formula (7) with the numerical results, we have employed the method of Bender and Wu[2] to calculate $A_0,\ldots,A_4$. Our results are summarized in Table I. The closeness of A_0 to 1 indicates satisfactory agreement with the Bender-Wu formulas and we note that the largeness of A_1 makes the first-order corrections considerable for all values of the coefficients which we have calculated. However, with $A_0=1$ and A_1, A_2, A_3, A_4 as in Table I, Eq. (7) reproduces the exact results with better than 0.003%(0.009%) accuracy for the case I(II) for $n\geq53$.

We have Padé-summed the perturbation series to obtain accurate estimates for the energies $E^{\mathrm{I,II}}(B)$ for $B\lesssim0.1$ a.u. Our results show no level crossing contrary to a statement in Praddaude[11] that "$3s$-$3d$" cross for $0.03<B<0.04$ in a.u. Since our Padé results also agree with a variational calculation which we have performed, we must conclude that the above-mentioned result of Praddaude is incorrect. Further details will appear in a forthcoming paper.[9]

To summarize, the two main results of this note are (i) the Bender-Wu asymptotic formula, Eq. (7), and (ii) the large-order perturbation calculation for the degenerate $3s$-$3d$ level of hydrogen in a magnetic field. The two agree with each other.

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