Second-order perturbative calculation of hydrogenic Zeeman levels

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The degenerate perturbative treatment of the hydrogenic Zeeman problem is put on a more rigorous basis and is extended to higher levels belonging to the manifolds of $M=n-|m|\leq 4$ basis states. The 16 $n=4$ levels are calculated and the large-n behavior of the basis states is discussed.

Degenerate perturbation theory has been applied to the calculation of 14 low-lying energy levels to the second order of the hydrogen atom in a homogeneous magnetic field.[1] We now generalize and extend the treatment to higher levels. Instead of the parabolic states, we use in the present work the definite-parity states, which are even and odd combinations of pairs of parabolic states, defined by Clark[2] as the basis states. The unperturbed hydrogenic states are, in fact, linear combinations of the Clark states. It will be seen that the zeroth-order states which diagonalize the first-order perturbation matrix are also their linear combinations.[3] For a given principal quantum number $n=n_1+n_2+|m|+1$, there are $M=n-|m|$ Clark states. When M is odd, the Clark states for $n_1=n_2$ are simply the parabolic states themselves. The first-order perturbation matrix is an $M\times M$ matrix consisting of two tridiagonal matrices of dimensions $\frac{1}{2}M\times\frac{1}{2}M$ if M is even or $\frac{1}{2}(M+1)\times\frac{1}{2}(M+1)$ and $\frac{1}{2}(M-1)\times\frac{1}{2}(M-1)$ if M is odd. This feature facilitates considerably the calculation of the first-order eigenvalues. The results for $M=2,3,4$ are given below.

(a) $M=2$ $(m=n-2,\ n_1-n_2=1)$. The parabolic states relevant to this case are $|1\rangle=|01m\rangle$ and $|2\rangle=|10m\rangle$. Consequently, we have the following two Clark states:

$$|C_1\rangle=2^{-1/2}(|1\rangle+|2\rangle)\ , \tag{1}$$

$$|C_2\rangle=2^{-1/2}(|1\rangle-|2\rangle)\ . \tag{2}$$

The matrix elements $M_{ij}^{(p)}$ of the pth order with respect to the parabolic states i and j can be obtained from the following expressions:[4]

$$M_{ii}^{(1)}=4n(3n^2+1-m^2-3q^2),\quad q=n_1-n_2\ , \tag{3}$$

$$M_{ij}^{(1)}=4n(n^2-m^2),\quad q=1\ , \tag{4}$$

$$M_{ii}^{(2)}=(-1106n^5-1316n^3-234n+1692n^3q^2 -586nq^4+388nq^2+132m^2nq^2+796m^2n^3 +356m^2n-122m^4n)/3,\quad q=n_1-n_2\ , \tag{5}$$

$$M_{ij}^{(2)}=(-572n^5-320n^3+662m^2n^3 +320m^2n-92m^4n)/3,\quad q=1\ . \tag{6}$$

Substituting the values of $m=n-2$ and $q=1$, we obtain

$$M_{11}^{(1)}=8n(n+3)(n-1)\ , \tag{7}$$

$$M_{12}^{(1)}=16n(n-1)\ , \tag{8}$$

$$M_{11}^{(2)}=16n(-27n^4-138n^3+70n^2+122n-27)/3\ , \tag{9}$$

$$M_{12}^{(2)}=2n(-n^4-956n^3+220n^2+832n-96)/3\ . \tag{10}$$

The matrix elements with respect to the Clark states can be obtained from the matrix elements $M_{ij}^{(p)}$. In the present case, the 2×2 first-order perturbation matrix in the Clark basis is diagonal. Consequently, the first-order eigenvalues are the diagonal matrix elements $M_{11}^{(1)}\ \pm M_{12}^{(1)}$ and they are

$$\lambda_{\rm I}^{(1)}=8n(n+5)(n-1)\ , \tag{11}$$

$$\lambda_{\rm II}^{(1)}=8n(n^2-1)\ , \tag{12}$$

corresponding to the eigenstates

$$|{\rm I}\rangle=|C_1\rangle\ , \tag{13}$$

$$|{\rm II}\rangle-|C_2\rangle\ . \tag{14}$$

The second-order eigenvalues are then found to be

$$\lambda_{\rm I}^{(2)}=2n(-217n^4-2060n^3+780n^2+1808n-312)/3\ , \tag{15}$$

$$\lambda_{\rm II}^{(2)}=2n(-215n^4-148n^3+340n^2+144n-120)/3\ . \tag{16}$$

(b) $M=3$ $(m=n-3,\ n_1-n_2=0,2)$. There are three parabolic states: $|1\rangle=|02m\rangle$, $|2\rangle=|20m\rangle$, and $|3\rangle=|11m\rangle$, and the resulting Clark states are

$$|C\rangle=2^{-1/2}(|1\rangle+|2\rangle)\ , \tag{17}$$

$$|C_2\rangle=|3\rangle\ , \tag{18}$$

$$|C_3\rangle=2^{-1/2}(|1\rangle-|2\rangle)\ . \tag{19}$$

Using Eqs. (3) and (5), we obtain

$$M_{11}^{(1)}=8n(n+5)(n-2)\ , \tag{20}$$

$$M_{33}^{(1)}=8n(n+4)(n-1)\ , \tag{21}$$

$$M_{11}^{(2)}=16n(-9n^4-69n^3+144n^2+164n-208)\ , \tag{22}$$

$$M_{33}^{(2)}=16n(-9n^4-69n^3-8n^2+230n-144)\ . \tag{23}$$

Using the nonvanishing matrix elements of the perturbation in I, we also find that[5]

$$M_{12}^{(1)}=0\ , \tag{24}$$

$$M_{13}^{(1)}=16n[2(n-2)(n-1)]^{1/2}\ , \tag{25}$$

$$M_{12}^{(2)}=-576n(n-2)(n-1)\ , \tag{26}$$

$$M_{13}^{(2)}=16(-41n^3-40n^2+57n+6)[2(n-2)(n-1)]^{1/2}\ . \tag{27}$$

The first-order eigenvalues are found to be

$$\lambda_{\rm I,II}^{(1)}=8n(n^2+3n-7)\pm 8nR,\quad R=(16n^2-48n+41)^{1/2}\ , \tag{28}$$

$$\lambda_{\rm III}^{(1)}=8n(n+5)(n-2)\ , \tag{29}$$

and the corresponding eigenstates that diagonalize the first-order perturbation matrix are[6]

$$|\mathrm{I}\rangle = a_1|C_1\rangle + a_2|C_2\rangle \ , \quad (30)$$

$$|\mathrm{II}\rangle = a_2|C_1\rangle - a_1|C_2\rangle \ , \quad (31)$$

$$|\mathrm{III}\rangle = |C_3\rangle \ , \quad (32)$$

where

$$a_1 = 4(n^2-3n+2)^{1/2}/(2R^2+6R)^{1/2} \ , \quad (33)$$

$$a_2 = (3+R)/(2R^2+6R)^{1/2} \ . \quad (34)$$

The second-order eigenvalues are therefore

$$\lambda_{\mathrm{I}}^{(2)} = a_1^2 A + a_2^2 B + 2(2)^{1/2} a_1 a_2 C \ , \quad (35)$$

$$\lambda_{\mathrm{II}}^{(2)} = a_2^2 A + a_1^2 B - 2(2)^{1/2} a_1 a_2 C \ , \quad (36)$$

$$\lambda_{\mathrm{III}}^{(2)} = M_{11}^{(2)} - M_{12}^{(2)} \ , \quad (37)$$

where

$$A = M_{11}^{(2)} + M_{12}^{(2)} \ , \quad (38)$$

$$B = M_{33}^{(2)} \ . \quad (39)$$

(c) $M=4$ ($m=n-4$, $n_1-n_2=1,3$). The four parabolic states for this case are $|1\rangle = |03m\rangle$, $|2\rangle = |30m\rangle$, $|3\rangle = |12m\rangle$, and $|4\rangle = |21m\rangle$, and the Clark states are

$$|C_1\rangle = 2^{-1/2}(|1\rangle + |2\rangle) \ , \quad (40)$$

$$|C_2\rangle = 2^{-1/2}(|3\rangle + |4\rangle) \ , \quad (41)$$

$$|C_3\rangle = 2^{-1/2}(|1\rangle - |2\rangle) \ , \quad (42)$$

$$|C_4\rangle = 2^{-1/2}(|3\rangle - |4\rangle) \ . \quad (43)$$

Equations (3)–(5) give in this case

$$M_{11}^{(1)} = 8n(n^2+4n-21) \ , \quad (44)$$

$$M_{33}^{(1)} = 8n(n^2+4n-9) \ , \quad (45)$$

$$M_{34}^{(1)} = 32n(n-2) \ . \quad (46)$$

Using the matrix elements given in the Appendix of I, we obtain the remaining matrix elements as follows:

$$M_{13}^{(1)} = 16n[3(n-3)(n-1)]^{1/2} \ , \quad (47)$$

$$M_{11}^{(2)} = 16n(-27n^4-276n^3+1030n^2+1180n-3171)/3 \ , \quad (48)$$

$$M_{33}^{(2)} = 16n(-27n^4-276n^3+118n^2+1708n-1491)/3 \ , \quad (49)$$

$$M_{12}^{(2)} = 0 \ , \quad (50)$$

$$M_{13}^{(2)} = 8n(-285n^2-368n+192)[3(n-3)(n-1)]^{1/2}/3 \ , \quad (51)$$

$$M_{14}^{(2)} = -576n(n-2)[3(n-3)(n-1)]^{1/2} \ , \quad (52)$$

$$M_{34}^{(2)} = -128n(n-2)(30n^2+46n-73)/3 \ . \quad (53)$$

The first-order eigenvalues are

$$\lambda_{\mathrm{I,II}}^{(1)} = 8n(n^2+6n-19) \pm 16nS, \quad S=(4n^2-10n+10)^{1/2} \ , \quad (54)$$

$$\lambda_{\mathrm{III,IV}}^{(1)} = 8n(n^2+2n-11) \pm 16nT, \quad T=(4n^2-22n+34)^{1/2} \ , \quad (55)$$

and the corresponding eigenstates are

$$|\mathrm{I}\rangle = b_1|C_1\rangle + b_2|C_2\rangle \ , \quad (56)$$

$$|\mathrm{II}\rangle = b_2|C_1\rangle - b_1|C_2\rangle \ , \quad (57)$$

$$|\mathrm{III}\rangle = d_1|C_3\rangle + d_2|C_4\rangle \ , \quad (58)$$

$$|\mathrm{IV}\rangle = d_2|C_3\rangle - d_1|C_4\rangle \ , \quad (59)$$

where

$$b_1 = [3(n^2-4n+3)]^{1/2}/[2S^2+2(n+1)S]^{1/2} \ , \quad (60)$$

$$b_2 = (n+1+S)/[2S^2+2(n+1)S]^{1/2} \ , \quad (61)$$

$$d_1 = [3(n^2-4n+3)]^{1/2}/[2T^2-2(n-5)T]^{1/2} \ , \quad (62)$$

$$d_2 = (-n+5+T)/[2T^2-2(n-5)T]^{1/2} \ . \quad (63)$$

The second-order eigenvalues are given by

$$\lambda_{\mathrm{I}}^{(2)} = b_1^2 P + b_2^2 Q + 2(2)^{1/2} b_1 b_2 D \ , \quad (64)$$

$$\lambda_{\mathrm{II}}^{(2)} = b_2^2 P + b_1^2 Q - 2(2)^{1/2} b_1 b_2 D \ , \quad (65)$$

$$\lambda_{\mathrm{III}}^{(2)} = d_1^2 P + d_2^2 Q + 2(2)^{1/2} d_1 d_2 D \ , \quad (66)$$

$$\lambda_{\mathrm{IV}}^{(2)} = d_2^2 P + d_1^2 Q - 2(2)^{1/2} d_1 d_2 D \ , \quad (67)$$

where

$$P = M_{11}^{(2)} + M_{12}^{(2)} \ , \quad (68)$$

$$Q = M_{33}^{(2)} + M_{34}^{(2)} \ , \quad (69)$$

$$D = M_{13}^{(2)} + M_{14}^{(2)} \ . \quad (70)$$

The above results are valid for all values of n. We have used these results to calculate the 16 $n=4$ levels. The numerical results are given in Table I. The $4e(\pm 3)$ levels are nondegenerate. Their eigenvalues $\lambda^{(p)}$ can be obtained directly from Eqs. (3) and (5) with $q=0$. In order to assign the eigenvalues and to identify hydrogenic levels, the hydrogenic states are expressed in terms of the corresponding eigenstates $|\mathrm{I}\rangle$, $|\mathrm{II}\rangle$, etc. For example, for $n=4$ and $m=0$, we have, by using Eqs. (40)–(43) and (56)–(64), the following:

$$|4s\rangle = 0.8702|\mathrm{I}\rangle + 0.4927|\mathrm{II}\rangle \ ,$$

$$|4d(0)\rangle = -0.4927|\mathrm{I}\rangle + 0.8702|\mathrm{II}\rangle \ ,$$

$$|4p(0)\rangle = 0.9545|\mathrm{III}\rangle + 0.2982|\mathrm{IV}\rangle \ ,$$

$$|4e(0)\rangle = -0.2982|\mathrm{III}\rangle + 0.9545|\mathrm{IV}\rangle \ .$$

Accordingly, we have the assignments λ_{I} to $4s$, λ_{II} to $4d(0)$, λ_{III} to $4p(0)$, and λ_{IV} to $4e(0)$.

Since the matrix elements $M_{13}^{(p)}$ were not included in the calculation of the three levels $3s$, $3p(0)$, and $3d(0)$ in I, we have recalculated the energy of these three levels. Noting that

$$|3s\rangle = 0.9156|\mathrm{I}\rangle + 0.4021|\mathrm{II}\rangle \ ,$$

$$|3d(0)\rangle = -0.4021|\mathrm{I}\rangle + 0.9156|\mathrm{II}\rangle \ ,$$

$$|3p(0)\rangle = |\mathrm{III}\rangle \ ,$$

we have the assignments λ_{I} to $3s$, λ_{II} to $3d(0)$, and λ_{III} to

TABLE I. Eigenvalues, coefficients, and energy levels. The Rayleigh-Schrödinger coefficients E_p and the energy E are calculated with the use of formulas given in Sec. III of Ref. 1. In Eq. (7) of Ref. 1, the coefficient λ_p is now $\lambda^{(p)}$ and the quantity in the bracket should be corrected to read $B^2\lambda^4/32$.

					E			
					$B=0.1$		$B=1.0$	
$nl\|m\|$	$\lambda^{(1)}$	$\lambda^{(2)}$	E_1	E_2	$m\leq 0$	$m>0$	$m\leq 0$	$m>0$
433	640	−263 640	320	−4 340 480	−0.159 87	+1.411 03	−1.507 67	+1.492 33
422	894	−449 688	447	−6 396 290	−0.09 816	+0.10 184	−0.999 994	+1.000 006
432	480	−157 933	240	−2 751 232	−0.10 874	+0.09 126	−1.01 030	+0.98 970
411	999.9	−549 701	500	−7 592 422	−0.049 98	+0.050 02	−0.498 35	+0.501 65
431	344.1	−70 675	172	−1 077 562	−0.056 89	+0.043 11	−0.503 81	+0.496 19
421	576	−240 128	288	−4 366 336	−0.063 21	+0.036 79	−0.512 26	+0.487 74
400	1045.2	−627 797	523	−9 165 072	−0.002 75		−0.001 46	
420	298.8	−83 662	149	−1 784 305	−0.019 52		−0.018 75	
410	618.4	−584 103	309	-14 867 105	−0.024 92		−0.024 82	
430	213.6	−127 363	107	−3 619 374	−0.028 17		−0.028 10	
300	417.6	−140 056	157	−537 083	−0.018 54		−0.010 01	
320	110.3	−13 646	41	−65 061	−0.038 10		−0.029 35	
310	192	−45 120	72	−225 990	−0.037 28		−0.032 68	

$3p(0)$. The results in Table I show that the two levels $3s$ and $3d(0)$ do not cross.[7] The results also show that the levels $3p(0)$ and $3d(0)$ cross at $B=0.1245$.[8]

High Rydberg states of an atom in a magnetic field have been of recent interest.[9] Results obtained by first-order classical perturbation theory for magnetic fields up to 6 T have been verified by exact numerical calculations. Our results show that, as n tends to infinity, the M states $|\mathrm{I}\rangle$, $|\mathrm{II}\rangle, \ldots,$ within the manifold tend to be hydrogenic. For example, it can be shown for $M=4$

$$|n,\ n-4,\ n-4\rangle = 2^{-1/2}(A_1|C_1\rangle + A_2|C_2\rangle) \rightarrow \tfrac{1}{2}|C_1\rangle + (3^{1/2}/2)|C_2\rangle \rightarrow |\mathrm{I}\rangle\ ,$$

$$|n,\ n-3,\ n-4\rangle = 2^{-1/2}(A_3|C_3\rangle + A_4|C_4\rangle) \rightarrow (3^{1/2}/2)|C_3\rangle + \tfrac{1}{2}|C_4\rangle \rightarrow |\mathrm{III}\rangle\ ,$$

$$|n,\ n-2,\ n-4\rangle = 2^{-1/2}(A_2|C_1\rangle - A_1|C_2\rangle) \rightarrow -(3^{1/2}/2)|C_1\rangle - \tfrac{1}{2}|C_2\rangle \rightarrow |\mathrm{II}\rangle\ ,$$

$$|n,\ n-1,\ n-4\rangle = 2^{-1/2}(A_4|C_3\rangle - A_3|C_4\rangle) \rightarrow \tfrac{1}{2}|C_3\rangle - (3^{1/2})/2|C_4\rangle \rightarrow |\mathrm{IV}\rangle\ ,$$

where[10]

$$A_1=(n-1)^{1/2}/(2n-5)^{1/2},\quad A_2=3^{1/2}(n-3)^{1/2}/(2n-5)^{1/2}\ ,$$

$$A_3=3^{1/2}(n-1)^{1/2}/(2n-3)^{1/2},\quad A_4=(n-3)^{1/2}/(2n-3)^{1/2}\ .$$

Clearly, our method is useful for the calculation of energy levels for all the states within the manifold M and for the study of level crossings.

[1] A. C. Chen, Phys. Rev. A 28, 280 (1983) (referred to hereafter as I).

[2] C. W. Clark, Phys. Rev. A 24, 605 (1981). See also M. L. Zimmerman, R. G. Hulet, and D. Kleppner, Phys. Rev. A 27, 2731 (1983).

[3] B. G. Adams, J. E. Avron, J. Cizek, and J. Paldus [Phys. Rev. A 21, 1914 (1980)] identified these states as tunneling states.

[4] Equations (16), (19), (17), and (20), respectively, in Ref. 1.

[5] In I, $M_{13}^{(2)}$ belonging to this case was not included in the calculation of the $3s$, $3p(0)$, and $3d(0)$ levels.

[6] $|\mathrm{I}\rangle$ and $|\mathrm{II}\rangle$ are the tunneling states defined in Ref. 3.

[7] This result is in agreement with the conclusion reached in Ref. 3.

[8] This differs from the conclusion in I as a result of switching the $3s$ and $3d(0)$ levels in accordance with the identification procedure discussed in this paper.

[9] J. B. Delos, S. K. Knudson, and D. W. Noid, Phys. Rev. Lett. 50, 579 (1983).

[10] These coefficients can be obtained with the help of C. B. Tarter, J. Math. Phys. 11, 3192 (1970).