Hidden crossings and the separation constant of a hydrogenlike atom in spheroidal coordinates

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(Received 18 October 1994)

Considered as a limiting case of a highly asymmetric two-Coulomb-center problem, the analytic properties of the eigenvalues of the constant of motion allowing separation of variables for a hydrogenlike atom in spheroidal coordinates are studied. Calculations of the positions of the branch points of the eigenvalues in the complex plane of internuclear separations are performed. It is found that they form characteristic series whose limiting points can well be predicted by semiclassical quantization conditions.

PACS number(s): 34.20.Cf

It is well known that in the two-Coulomb-center problem (Z_1,e,Z_2), the properties of the analytically continued potential-energy curves into the complex plane of internuclear separations R play an important role in the adiabatic description of the slow one-electron colliding systems [1]. The exact degeneracies of the energy eigenvalues in the complex R plane correspond to branch points of a multivalued analytic function describing the energies of all states of a given symmetry. The position (i.e., real and imaginary parts) of a branch point is directly related to transition probabilities between various adiabatic states [1]. When the imaginary part of a branch point is small, the potential-energy curves exhibit sharp avoided crossings for real values of R, whereas when located further away from the real R axis branch points are usually referred to as "hidden crossings."

Recent theoretical investigations of the highly asymmetric systems $Z_2 \gg Z_1$ [2] have revealed a type of branch points which form the so-called H series. These branch points connect the energy surfaces labeled by (k,q,m) and $(k-1,q+1,m)$ in standard notation of spheroidal quantum numbers [3]. These singularities are expected to remain in the limit $Z_1 \to 0$, $Z_2 = Z$, so that they should show up in the one-center problem of hydrogenlike atoms with variables separated in spheroidal coordinates. However, the energies are, in this case (we use atomic units $|e| = m_e = \hbar = 1$ throughout the work), $E_n = -Z^2/(2n^2)$ $(n = k+q+m+1$ and we assume $m > 0$ since it enters all formulas below as $m^2)$ and they do not depend on R, which plays the role of a parameter defining the coordinate system. Nevertheless, the eigenvalues $\lambda(R)$ that depend on R are those of the separation constant [3,4]

$$\Lambda = L^2 + \frac{ZR}{n} A_z \ , \tag{1}$$

where L is the orbital angular momentum operator and A_z is the z component of the Runge-Lenz vector. Together with the Hamiltonian H and L_z the operator Λ forms the complete set of commuting observables defining the states of a hydrogenlike atom with variables separated in spheroidal coordinates.

The eigenvalues $\lambda_{kqm}(R)$ can be found by diagonalizing (1), for example, in the spherical basis $|nlm\rangle$ of a hydrogenlike atom. With the help of matrix elements

$$\langle nlm|A_z|nl+1m\rangle = \langle nl+1m|A_z|nlm\rangle = \left\{ \frac{[n^2-(l+1)^2][(l+1)^2-m^2]}{(2l+1)(2l+3)} \right\}^{1/2} \tag{2}$$

the corresponding three-diagonal determinant can be expressed, by using standard methods [3], in terms of continued fractions. The particularly convenient form of the secular equation is

$$\lambda = l(l+1) + \frac{B_{l-1}}{A_{l-1}+} \frac{B_{l-2}}{A_{l-2}+} \cdots \frac{B_m}{A_m} + \frac{B_l}{A_{l+1}+} \frac{B_{l+1}}{A_{l+2}+} \cdots \frac{B_{n-2}}{A_{n-1}} \ , \tag{3}$$

where

$$A_l = l(l+1) - \lambda \ , \tag{4}$$

$$B_l = -(ZR)^2 \frac{(l+1)^2-m^2}{(2l+1)(2l+3)} \left[1 - \left[\frac{l+1}{n} \right]^2 \right] . \tag{5}$$

For fixed n and m relation (3) is a polynomial equation with $n-m$ roots: λ_{kqm} $(q = 0,1,\ldots,n-m-1$; $k = n-m-q-1)$. It can be solved for real as well as for complex values of R and therefore perform a desired analytic continuation of the eigenvalues $\lambda_{kqm}(R)$ into the complex R plane.

For small values of ZR, the following result, which can also be obtained by applying perturbation theory to the operator Λ, immediately follows from (3):

$$\lambda_{kqm}=l(l+1)-\frac{(ZR)^2}{2(2l+1)}\left\{\frac{(l+1)^2-m^2}{(l+1)(2l+3)}\left[1-\left[\frac{l+1}{n}\right]^2\right]-\frac{l^2-m^2}{l(2l-1)}\left[1-\left[\frac{l}{n}\right]^2\right]\right\}+O((ZR)^4)\ , \tag{6}$$

where $l=q+m$ is the "united atom" spherical quantum number. We note that expansion (6) (in all orders) does not contain any logarithmic terms, as opposed to the similar expansion in the two-Coulomb-center problem [3].

The case $m=n-1$ is a trivial one, since then the eigenvalues $\lambda_{00n-1}=(n-1)n$ are R independent. When $m=n-2$, the subspace is two dimensional; the two roots of the quadratic equation (3) define two branches $\lambda_{10n-2}(ZR)$ and $\lambda_{01n-2}(ZR)$ of a double-valued analytic function of a complex variable ZR with branch points (points of exact degeneracy of the eigenvalues) located at

$$ZR=\pm in(n-1)\ . \tag{7}$$

In all other cases the search for the points of degeneracy in the complex plane of the variable ZR has to be performed by means of numerical solution of the secular equation (3). The calculations show that there are indeed the branch points which connect the eigenvalues λ_{kqm} with $\lambda_{k-1q+1m}$. For fixed q and m and a variable k (i.e., n) these branch points are grouped in such a way that they form series which we label as H^s_{qm} and show in Fig. 1. For each of the series we show the first three members (open circles) corresponding to $k=1$, 2, and 3 (or $n=q+m+2$, $q+m+3$, and $q+m+4$) and the limiting branch point (full circles) toward which the members of the series converge when $k\to\infty$ (i.e., $n\to\infty$). In the latter case one has to deal with the infinite continuous fraction in Eq. (3). The superscript $s=0,1,\ldots$ distinguishes between the H^s_{qm} series which appear in different regions of the ZR plane. Only the first quadrant is shown because the pattern is symmetric with respect to both the real and imaginary axes. This is the combined consequence of the Schwartz reflection principle of analytic continuation $\lambda(ZR^*)=\lambda^*(ZR)$ and the symmetry property $\lambda(-ZR)=\lambda(ZR)$.

From the data presented in Fig. 1 the overall structure and distribution of branch points in complex ZR plane can be inferred. We note also that the positions of the branch points define the convergence radii of the united-atom series expansions, the first two terms of which are given in Eq. (6).

Another question of general importance which we have studied is to what extent the semiclassical conditions of quantization contain the information on analytic properties of the eigenvalues when analytically continued in the complex plane of a parameter. We shall restrict ourselves here to the determination of the limiting branch points of the H^s_{qm} series. By using the results of Ref. [5], the semiclassical quantization condition for determining the eigenvalues λ in the limit of $k\to\infty$ ($n\to\infty$) is

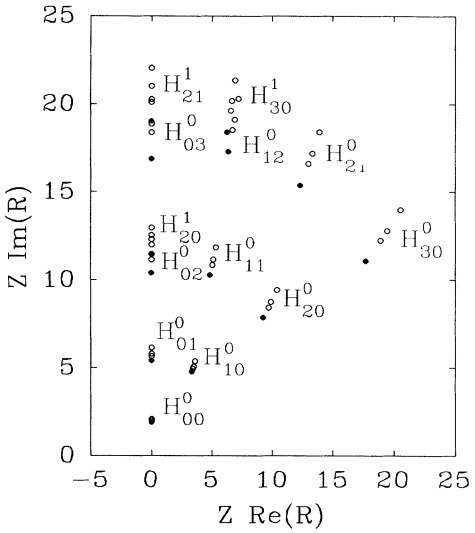

FIG. 1. H^s_{qm} series of branch points where $\lambda_{kqm}=\lambda_{k-1q+1m}$, for $k=1,2,3$ (open circles) and $k\to\infty$ (full circles).

$$2(\lambda+a)^{1/2}E\left[\frac{2a}{\lambda+a}\right]=\pi\left[q+\frac{1}{2}+\frac{3m}{4}\right]+\gamma(1-\ln\gamma)+\frac{1}{2i}\ln\frac{\Gamma\left[\frac{m+1}{2}+i\gamma\right]}{\Gamma\left[\frac{m+1}{2}-i\gamma\right]}\ , \tag{8}$$

where $a=ZR$ and

$$\gamma=\frac{2}{\pi}(\lambda+a)^{1/2}\left[K\left[\frac{\lambda-a}{\lambda+a}\right]-E\left[\frac{\lambda-a}{\lambda+a}\right]\right]\ . \tag{9}$$

Above, $K(z)$ and $E(z)$ are complete elliptic integrals as defined in [6]. The quantization condition (8) is uniform with respect to the passage of the critical point $\lambda=a$. A comparison with the exact quantum results for real values of ZR is demonstrated in Fig. 2. The overall agreement is very good, although the behavior in the close vicinity of the united atom limit is quite different from (6). The leading terms of the iterative solution of (8) obtained for small values of ZR are given by

$$\lambda\simeq(l+\tfrac{1}{2})^2-\frac{\mu^2-\mu+\frac{1}{6}}{\ln\frac{8(l+\frac{1}{2})^2}{ZR}-2}\ , \tag{10}$$

where $l=q+m$ and $\mu=(m+1)/2$. The above function has an infinite derivative at $ZR=0$, although the limit itself is correct [within the semiclassical substitution $l(l+1)\to(l+\frac{1}{2})^2$].

When solving Eq. (8) for λ with complex values of $a=ZR$, care must be taken to avoid any jumps in multivalued functions which are present in (8) (i.e., the square root, logarithms, and elliptic integrals). If this is done then the set of limiting branch points for the H^s_{qm} series is

TABLE I. Positions of the limiting branch points ($k \to \infty$) for a selection of H^s_{qm} series. Quantum results, [Re(ZR),Im(ZR)]; semiclassical results, (Re(ZR),Im(ZR)).

(m,s)	$q=0$	$q=1$	$q=2$	$q=3$
(0,0)	[0.0000, 1.899]	[3.330, 4.776]	[9.265, 7.860]	[17.73, 11.09]
	(−0.052, 1.859)	(3.283, 4.763)	(9.216, 7.848)	(17.69, 11.08)
(0,1)			[0.0000, 11.45]	[6.268, 18.41]
			(−0.054, 11.41)	(6.219, 18.39)
(2,0)	[0.000, 10.43]	[6.351, 17.30]	[15.38, 24.35]	[27.01, 31.60]
	(0.623, 10.93)	(6.925, 17.62)	(15.93, 24.59)	(27.55, 31,79)
(2,1)			[0.000, 28.16]	[9.227, 39,18]
			(0.609, 28.65)	(9.811, 39.54)

in very good agreement with exact quantum results, as shown in Fig. 3. The worst agreement is for the cases where $q < m$. This is understandable since the semiclassical quantization condition (8) is derived under the assumption $q \gg m$, so that the agreement obtained for small values of $q \geq m$ is surprisingly good. This is also illustrated in Table I, where a comparison between the quantum and semiclassical results is given for a number of typical cases.

Generally, the numerical solution of the semiclassical equation (8) is more difficult than that of the exact secular equation which itself does not contain any multivalued functions. The merit of the semiclassical approach is that often analytic estimates for the positions of the branch points can be obtained. An example is given in Ref. [5], where this is done for the so-called S series in the two-Coulomb-center problem. Unfortunately, in the present case of the H series such simple estimates do not seem to exist. Nevertheless, in the cases of H^0_{q0} series (which are the closest to the real R axis) one can derive a transcendental equation which approximately determines the positions of the limiting branch points. For that purpose we use the following two empirically [based on numerical solutions of Eq. (8)] established facts valid in the vicinity of a branch point: first, the argument of the elliptic integral in Eq. (8) is close to one and second, the argument of the Γ function, $\mu - i\gamma$, is close to zero, i.e., to the position of the pole. If we use the appropriate expansions, multiply Eq. (8) by $2i$, and take the exponent of both sides, we obtain

$$16u^3 e^{4iu-2} - iu^2 + u + 2ia = 0 , \tag{11}$$

where $u = (\lambda + a)^{1/2}$. This equation implicitly defines $u = u(a)$ [i.e., $\lambda = \lambda(a)$]. The quantum number q is absent from Eq. (11) as a result of taking the exponent of the original equation (8), but it reappears as a label of different solutions of Eq. (11). Now we are looking for the branch points where Eq. (11) has double solutions; therefore the derivative of (11) with respect to u should also be zero:

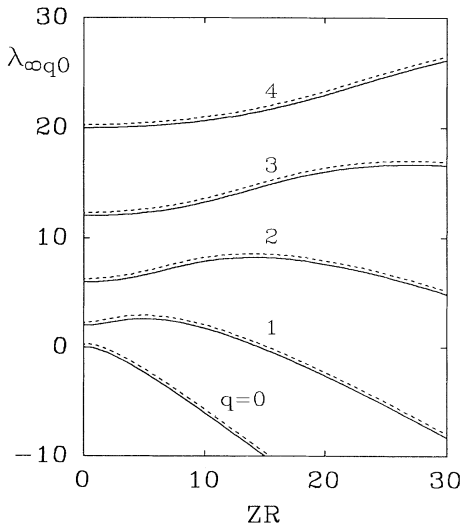

FIG. 2. Eigenvalues $\lambda_{\infty q0}(ZR)$ for real values of ZR. Quantum-mechanical calculations, full lines; semiclassical results, broken lines.

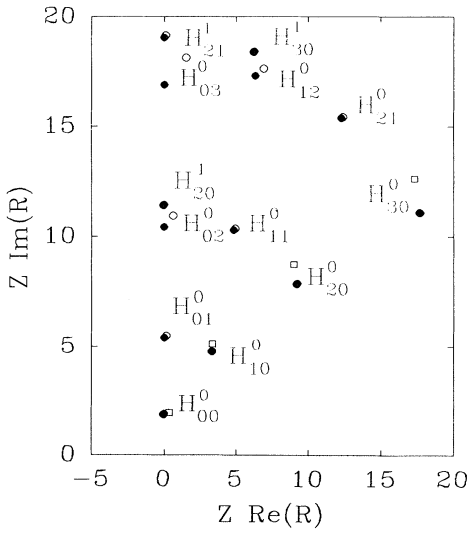

FIG. 3. Limiting branch points ($k \to \infty$) for H^s_{qm} series. Quantum results, full circles; semiclassical results, open circles; approximate semiclassical results, from Eqs. (11) and (12), open squares.

$$16(4iu+3)u^2e^{4iu-2}-2iu+1=0\ . \tag{12}$$

Solving numerically for u from (12) and substituting into (11) to find $a=ZR$ we obtain a series of branch points which are shown in Fig. 3 as open squares and are in good agreement with those obtained by numerical solution of Eq. (8). In the general case of H^s_{qm} series, one can impose the condition $\mu-i\gamma\simeq -s$ ($s=0,1,\ldots$); however, the results thus obtained, although qualitatively represent correctly the distribution of branch points, are quantitatively less accurate.

In conclusion, let us note that a pattern of branch points similar to that studied here is expected to be characteristic of all highly asymmetric ($Z_2 \gg Z_1$) two-Coulomb-center systems. In this case, of course, there will also be the branching of the energy eigenvalues (potential-energy surfaces). In slow collisions the H series of branch points would be responsible for the transitions between the quasimolecular states whose united-atom angular momentum quantum numbers differ by one, while the principal and magnetic quantum numbers are fixed. These transitions are expected to be relatively weak because the H series are comparatively distant from the real R axis.

T.P.G. is grateful for the support of this work by the Ministry of Science and Technology of the Republic of Serbia, Yugoslavia. E.A.S. acknowledges support from the International Atomic Energy Agency through Grant No. 7693/RB.

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