Quasicrossings of the energy terms in the two-Coulomb-centre problem

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Outline

- Relevance for the adiabatic theory of atom collisions
- The wave functions of $Z_1 e Z_2$ system
- Energy splitting: comparison of results
- Conclusions

The adiabatic approximation in atomic collision theory

In adiabatic approximation ($v_n \ll v_e$), solution of the Schrödinger equation

$$\hat{H}(\vec{R})\Psi(\vec{r},t) = i\frac{\partial \Psi}{\partial t} \tag{1}$$

is usually represented in the form

$$\Psi(\vec{r},t) = \sum_p g_p(t)\psi_p(\vec{r},R)\exp\left(-i\int^t E_p\left(R(vt')\right)dt'\right), \tag{2}$$

leading to Born-Fock equations [1] for $g_p(t)$

$$\frac{dg_p(t)}{d\tau} = \sum_{p'}{}' \left\langle \psi_p(\tau)\left|\frac{d}{d\tau}\right|\psi_{p'}(\tau)\right\rangle \exp\left(\frac{i}{v}\int^\tau \Delta E_{p\,p'}(\tau')\,d\tau'\right) g_{p'}(\tau'),$$

$$\tau = v\,t, \qquad \Delta E_{p\,p'}(\tau') = E_p(\tau) - E_{p'}(\tau),$$

The inelastic transition cross section then

$$\sigma_{pq} = 2\pi\int_0^\infty \lim_{t\to\infty}|g_p(t)|^2 d\rho. \tag{3}$$

[1] M. Born and V. A. Fock. Zeitschrift für Physik a Hadrons and Nuclei 51.3-4 (1928), pp. 165180.

The avoided crossings (simple theory)

In two-level system, the energy eigenvalues are of the form

$$E_{\pm} = \frac{E_1 + E_2}{2} \pm \frac{1}{2}\sqrt{(E_1 - E_2)^2 + 4W^2}. \qquad (4)$$

The graf $E = f(E_1 - E_2)$ is the two branches of a hyperbola at which curve asymptotically approaches the original unperturbed energy levels

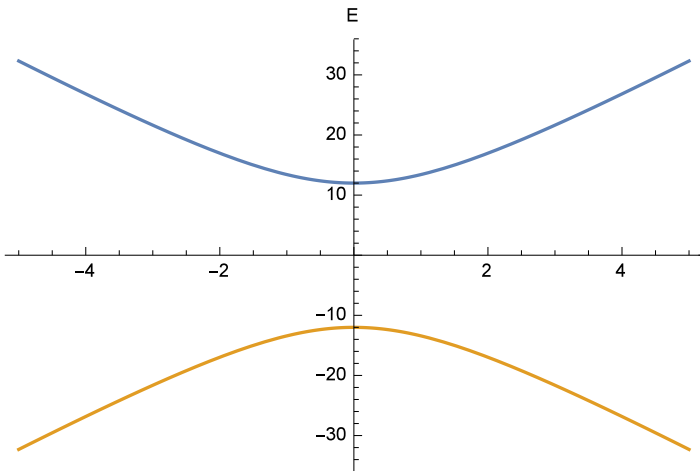


Figure: W=4

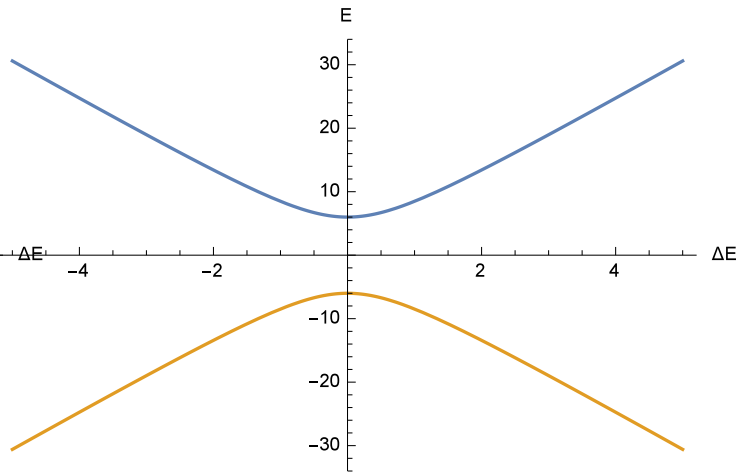
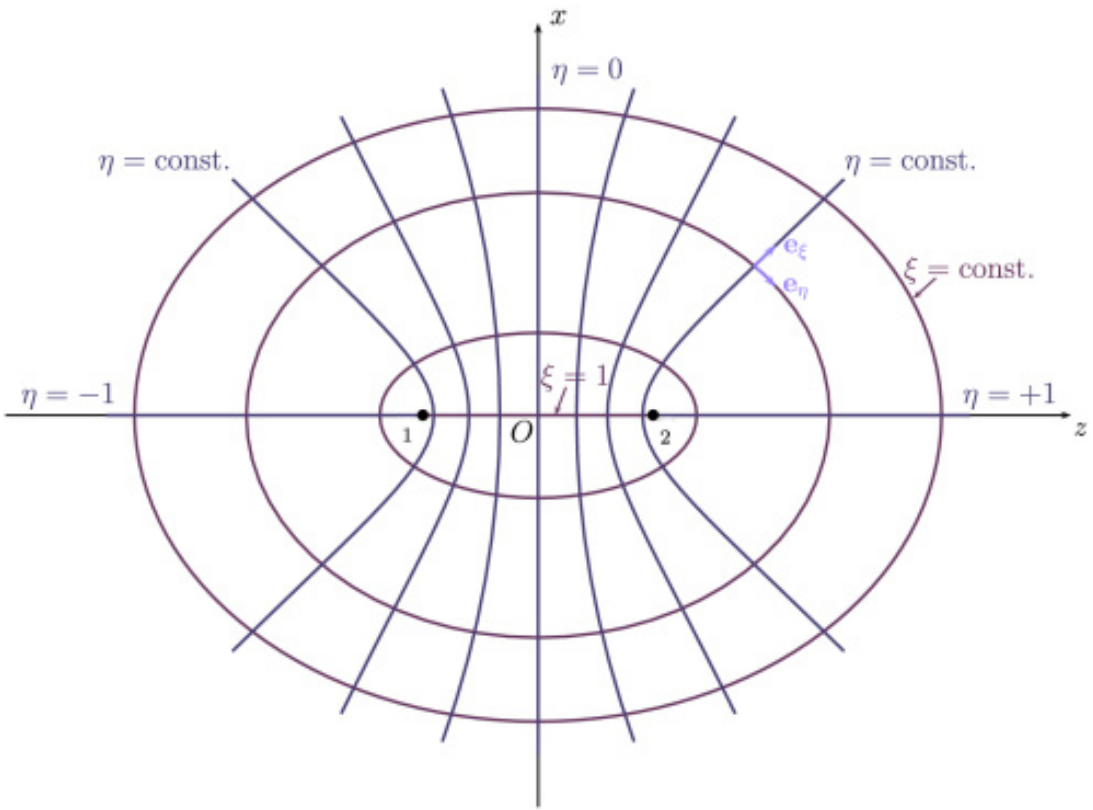


Figure: W=1

Important coordinate system for this problem

The prolate spheroidal coordinate system:

$$\xi = \frac{r_1 + r_2}{R}, \quad \eta = \frac{r_1 - r_2}{R}, \quad \phi = \arctan\frac{y}{x}, \tag{5}$$
$$\xi \in [1; \infty), \quad \eta \in [-1; 1], \quad \phi \in [0; 2\pi)$$



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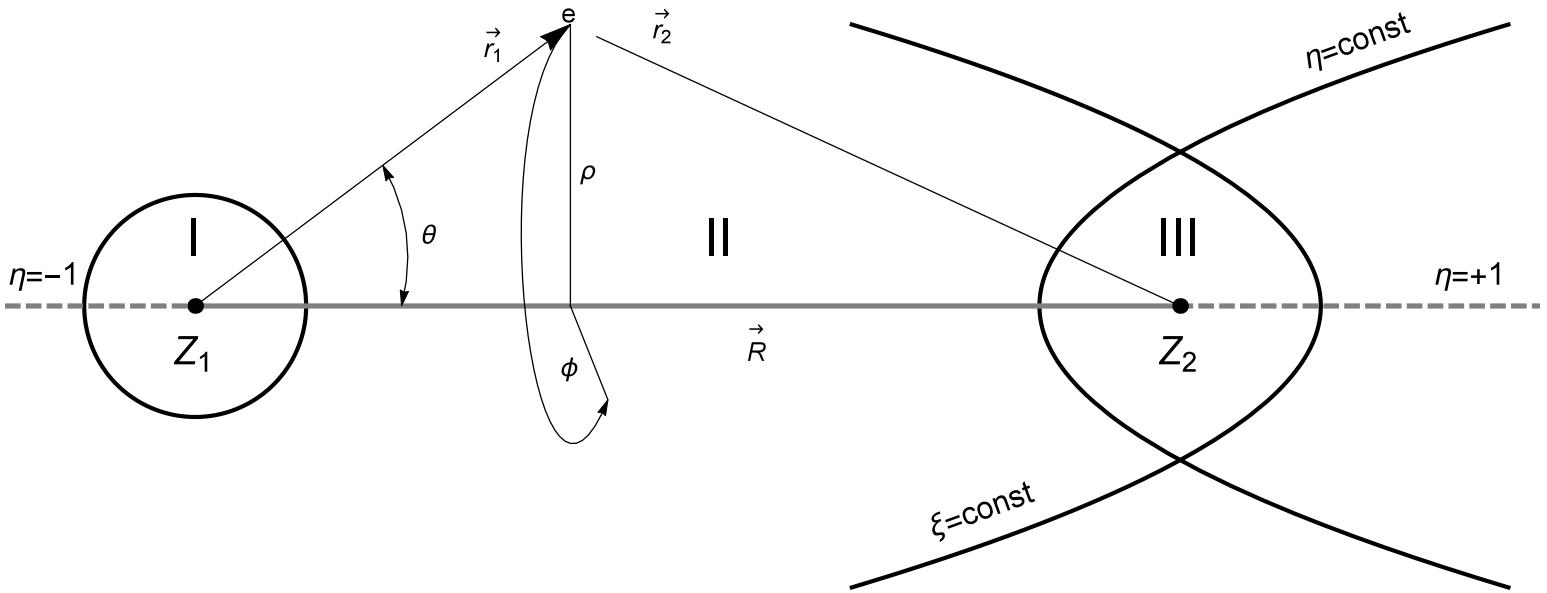

Solution of the two-Coulomb-centre problem

The wave function after the separation of variables has the form

$$\Psi(\vec{r}, R) = \frac{U(\xi, R)}{\sqrt{\xi^2 - 1}} \frac{V(\eta, R)}{\sqrt{1 - \eta^2}} \frac{e^{\pm im\phi}}{\sqrt{2\pi}} = \frac{\psi(\xi, \eta, R)}{\sqrt{(\xi^2 - 1)(1 - \eta^2)}} \frac{e^{\pm im\phi}}{\sqrt{2\pi}}. \quad (6)$$

Next, the shifted variables has been used:

$$\mu = \frac{R}{2}(\xi - 1), \quad \mu \in [0, \infty), \quad \nu = \frac{R}{2}(1 + \eta), \quad \nu \in [0, R]. \quad (7)$$

For $\mu \ll R$ (near the internuclear axis) and $\nu \ll R$ (near the left atomic core) the perturbation theory was used:

$$\psi^{pert}(\mu, \nu) = C(R)\, U^{pert}(\mu)\, V^{pert}(\nu),$$

$$U^{pert} = f^{(0)}_{n_1}(\mu) + \sum_{p=1}^{3} \sum_{k=-p}^{p} c^{(p)}_{n_1+k}(R^{-p}) f^{(0)}_{n_1+k}(\mu),$$

$$V^{pert} = f^{(0)}_{n_2}(\nu) + \sum_{p=1}^{3} \sum_{k=-p}^{p} c^{(p)}_{n_2+k}(R^{-p}) f^{(0)}_{n_2+k}(\nu),$$

$$f^{(0)}_{n_i}(x) = \left(\frac{(n_i+m)!}{n_i!(m!)^2(2n_i+m+1)} \right)^{1/2} (2\gamma x)^{(m+1)/2} e^{-\gamma x} F(-n_i,\, m+1,\, 2\gamma x).$$

Solution of the two-Coulomb-centre problem

In the internuclear region for the quasiangular part of the wave function a WKB approximation has been used ($\hbar = 1$):

$$V^{quas} = \frac{C_0}{\sqrt{q}} \exp\left[-\int_{\nu_2}^{\nu} q d\nu' + S_1 + S_2\right] \tag{8}$$

where the quasiclassical corrections S_1 and S_2 are determined by the formulae

$$\begin{aligned} S_1 = &-\frac{\tilde{Z}_1}{4\gamma^3\nu^2}\left(1+\frac{17\tilde{Z}_1}{6\gamma^2\nu}\right) + \frac{\tilde{Z}_2}{4\gamma^3(R-\nu)^2}\left(1+\frac{17\tilde{Z}_2}{6\gamma^2(R-\nu)}\right) \\ &+ \frac{m^2-1}{16\gamma^3}\left(\frac{1}{\nu^3}+\frac{1}{\nu^2 R}-\frac{1}{R(R-\nu)^2}-\frac{1}{(R-\nu)^3}\right) + \frac{\tilde{Z}_1\tilde{Z}_2}{2\gamma^5 R^3}\ln\frac{\nu}{R-\nu} \\ &+ \frac{\tilde{Z}_1\tilde{Z}_2}{4\gamma^5 R}\left(\frac{3}{(R-\nu)^2}-\frac{3}{\nu^2}+\frac{1}{R}\left[\frac{1}{R-\nu}-\frac{1}{\nu}\right]\right) + C_1, \end{aligned} \tag{9}$$

$$S_2 = \frac{\tilde{Z}_1}{4\gamma^4\nu^3} + \frac{\tilde{Z}_2}{4\gamma^4(R-\nu)^3} + C_2. \tag{10}$$

Solution of the two-Coulomb-centre problem

The final expression for two-Coulomb-centre wave function Ψ of $Z_1 e Z_2$ system has the form

$$\Psi\left(\vec{r}, R\right) = C(R) \frac{U^{pert}\left(\mu, R\right)}{\sqrt{\xi^2 - 1}} \frac{V^{quas}\left(\nu, R\right)}{\sqrt{1-\eta^2}} \frac{e^{\pm im\phi}}{\sqrt{2\pi}}. \tag{11}$$

This wave function has been used to calculate the exchange energy splitting ($A_i = 2n_i + m + 1$, $A'_i = 2n'_i + m + 1$):

$$\Delta E = \oint_S \left(\Psi_I \vec{\nabla} \Psi_{II} - \Psi_{II} \vec{\nabla} \Psi_I\right) d\vec{S} = \frac{2\gamma^2 (-1)^{n_2+n'_2} (2\gamma R)^{n_2+n'_2+m+1} \mathrm{e}^{-\gamma R}}{\left[n\, n'\, n_2!\, (n_2+m)!\, n'_2!\, (n'_2+m)!\right]^{1/2}} \times$$
$$\left\{1 - \frac{1}{2\gamma R}\left[\frac{A_2^2+A_2'^2}{4} + A_2 A'_2 + \frac{1-m^2}{2}\right] - \frac{A_2+A'_2}{2\gamma R} - \frac{A_1}{2\gamma^2 R}\left(\frac{Z_1}{n} + \frac{Z_2}{n'}\right)\right.$$
$$+ \frac{[A_2^2+A_2'^2+4A_2A'_2+2(1-m^2)]^2}{128\gamma^2 R^2} + \frac{A_2^3+A_2'^3+(A_2A'_2-4A_1+2m^2-6)(A_2+A'_2)}{32\gamma^2 R^2}$$
$$\left. + \frac{A_1(3A_1+1-m^2)}{4\gamma^2 R^2} + \frac{(A_1-1)(A_2+A'_2)^2+2A_2A'_2(A_1-2)}{8\gamma^2 R^2}\right\}. \tag{12}$$

Energy splitting: comparison of results

Table: Adiabatic energy splittings ΔE at quasicrossing points R_c in the system (p, e, Z_2); $a(-b)$ stands for $a \cdot 10^{-b}$

Z_2	$(Nlm) - (N'l'm')$	R_c	ΔE	ΔE_P [2]	ΔE_{num} [3]	ΔE_B [4]
4	$(4,3,0) - (3,2,0)$	7.76	6.66(−2)	6.56(−2)	6.94(−2)	–
5	$(5,4,0) - (4,3,0)$	12.92	4.07(−3)	6.09(−3)	4.25(−3)	4.16(−3)
6	$(6,5,0) - (5,4,0)$	21.4	2.40(−5)	3.37(−5)	–	2.41(−5)
7	$(7,6,0) - (6,5,0)$	31.9	2.06(−8)	2.44(−8)	–	2.14(−8)
8	$(8,7,0) - (7,6,0)$	44.3	3.04(−12)	4.51(−12)	–	2.88(−12)

[2] J.D. Power, Phil. Trans. Roy. Soc. London. Ser. A 274, 663 (1973).
[3] I.V. Komarov and N.F. Truskova, JINR Report No. P4-11445, (1978).
[4] A.A. Bogush and V.S. Otchik, J. Phys. A 30, 559 (1997).

Conclusions

- Using fully consisted scheme, the asymptotic wave functions for the $Z_1 e Z_2$ problem has been obtained
- The energy splitting ΔE at the psedocrossing points was calculated.
- A good agreement of our results for ΔE with the numerical and another asymptotical results has been obtained.
- Future plans: calculation of the two-electron exchange processes.

Thank you for attention