Part III.

Exact expansion around the asymmetric stationary point

Calculation of the coefficients of 1/*D*-expansion for two-electron atoms was done firstly in the paper [L. D. Mlodinow and N. Papanicolaou, *Ann. Phys. (N. Y.)* **131**, 1 (1981)] and later in [D. Z. Goodson and D. R. Herschbach, *Phys. Rev. Lett.* **58**, 1631 (1987)]. The present approach is similar to the second paper.

At the zero-order (classical electrostatic) approximation, it is necessary to find a stationary point of the effective potential. Finding the asymmetric-configuration stationary point was considered in the first section of this report. The large-dimensional limit equals to the value of the potential at the stationary point. For helium, it is $D^2 E \rightarrow E_0 = -10.616 - 2.117i$ (here, we use atomic units for energy that differ by Z^2 times from units used in the first section. Now, the Coulomb interaction reads $-Z/r_1 - Z/r_2 + 1/r_3$, not $-1/r_1 - 1/r_2 + \lambda/r_3$ as in the first section).

The first, second etc. orders of the expansion

$$
D^2 E \sim E_0 + E_1 D^{-1} + E_2 D^{-2} + \dots \tag{1}
$$

represent quantum corrections. The first coefficient is the energy of harmonic vibrations plus some additional term equal to $6E_0$ for our problem:

$$
E_1 = (n_1 + \frac{1}{2})\omega_1 + (n_2 + \frac{1}{2})\omega_2 + (n_3 + \frac{1}{2})\omega_3 + 6E_0
$$
 (2)

For helium, the frequencies are:

$$
\omega_1 = 47.167 + 22.993i
$$

\n
$$
\omega_2 = 58.670 - 16.752i
$$

\n
$$
\omega_3 = 9.053 + 17.137i
$$
 (3)

Note that the frequencies are Z^2 times more than in previous sections, because now we use different units. Note also that we interchange the first two frequencies to make our harmonic quantum numbers n_1 , n_2 , and n_3 equal to n , k , and l from the paper *K. Richter et al.* correspondingly. It can be seen from the table "Transformation to normal modes using prolate spherical coordinates" that the third

slowest mode corresponds to oscillation of $r₁$, the first mode is associated with oscillation of the coordinate $(r_1 - r_2) / r_3$, and the second mode is associated with oscillation of the coordinate $(r_1 + r_2)/r_3$ (taking into account that the first two mode are interchanged now). So, quantum numbers (n_1, n_2, n_3) equal to quantum numbers (n_1, n_1, l) derived from the adiabatic approximation that are in turn in one-to-one correspondence with the semiclassically derived set (n, k, l) , see the paper of K. *Richter et al*.

Higher coefficients of $1/D$ -expansion, E_2 , E_3 etc. represent anharmonic corrections. They were calculated by recurrence relations that follows from the expansion of the wavefunction over *D*^{−1/2} and over the set of harmonic-oscillator eigenfunctions. These recurrence relations contain only elementary arithmetic operations (sum, subtract, multiply, and divide), so we use the same program as for symmetric real minimum allowing complex-type variables. Results (including one anharmonic term) for several states of helium are:

 $E(0,0,0) = (-10.616 - 2.117i)D^{-2} + (-6.253 - 1.013i)D^{-3} + (-64.460 + 15.795)D^{-4} + ...$ $E(1,0,0) = (-10.616 - 2.117i)D^{-2} + (40.914 + 21.980i)D^{-3} + (-329.778 - 176.734)D^{-4} + ...$ $E(2,0,0) = (-10.616 - 2.117i)D^{-2} + (88.081 + 44.973i)D^{-3} + (-957.418 - 701.922)D^{-4} + ...$ $E(3,0,0) = (-10.616 - 2.117i)D^{-2} + (135.249 + 67.965i)D^{-3} + (-1947.379 - 1559.768)D^{-4} + ...$ $E(4,0,0) = (-10.616 - 2.117i)D^{-2} + (182.416 + 90.958i)D^{-3} + (-3299.662 - 2750.272)D^{-4} + ...$ $E(5,0,0) = (-10.616 - 2.117i)D^{-2} + (229.583 + 113.951i)D^{-3} + (-5014.267 - 4273.435)D^{-4} + ...$ $E(6,0,0) = (-10.616 - 2.117i)D^{-2} + (276.750 + 136.943i)D^{-3} + (-7091.193 - 6129.256)D^{-4} + ...$ $E(10,0,0) = (-10.616 - 2.117i)D^{-2} + (465.420 + 228.914i)D^{-3} + (-19022.116 - 16879.124)D^{-4} + ...$ $E(3,0,1) = (-10.616 - 2.117i)D^{-2} + (144.301 + 85.102i)D^{-3} + (-2052.318 - 2363.040)D^{-4} + ...$ $E(6,1,0) = (-10.616 - 2.117i)D^{-2} + (335.420 + 120.191i)D^{-3} + (-11053.041 - 5148.327)D^{-4} + ...$ (4)

Nineteen coefficients for (6,0,0) state are:

 (-10.61633515089777,-2.11689701804518) (276.7504091082661,136.9432964397447) (-7091.193389589787,-6129.255903391875) (269801.5025965456,256138.6161855411) (-1.353066840540659E+007,-1.088303340599514E+007) (6.848903587307632E+008,4.742266328011606E+008) (-3.127163526877386E+010,-2.010975915019004E+010) (1.187173493292221E+012,7.104015657159127E+011) (-2.795559457263984E+013,-6.483424665728123E+012) (-4.583529513030274E+014,-2.265024336321758E+015) (7.430140341903816E+016,2.895796762447328E+017) (2.661451087683579E+017,-2.157465392593928E+019) (-6.239289524988538E+020,9.146228439908465E+020) (7.655491183915015E+022,1.787257718989365E+022) (-2.111311501343495E+024,-9.891146614483248E+024) (-5.576986682904429E+026,6.533964036247258E+026) (5.780695906233375E+028,-3.882925836040120E+028) (-1.210026262811870E+031,-5.269155907072095E+030) (-8.856240072011069E+032,1.299751003660980E+033)

FORTRAN notation for complex numbers was used, i. e. we list here $(Re E_0, Im E_0)$, $(Re E_1, Im E_1)$,

..., $(Re E_{14}, Im E_{14})$.

Results of summation of this series for $D = 3$ are:

There is no convergence for Padé, quadratic, and Padé - Borel approximants. Instead of summing the series $E \sim E_0 D^{-2} + E_1 D^{-3} + E_2 D^{-4} + ...$ 1 3 $z^{-2} + E_1 D^{-3} + E_2 D^{-4} + ...$ we try to sum the *shifted* series $E \sim \widetilde{E}_0 (D+a)^{-2} + \widetilde{E}_1 (D+a)^{-3} + \widetilde{E}_2 (D+a)^{-4} + ...$ 1 3 $(a+a)^{-2} + \widetilde{E}_1(D+a)^{-3} + \widetilde{E}_2(D+a)^{-4} + \dots$. We obtained good results using a shift parameter $a = 2n₁ - 1$. The results for this shift parameter for the state (6,0,0) are given below.

Exact results of quantum-mechanical calculation of K. Richter et al. are given in the last two lines.

Another choice of the shift parameter is $a = -E_1 / (2E_0)$ that leads to $\tilde{E}_1 = 0$. So, the scaled energy $(D+a)^2 E$ is weakly dependent on $1/(D+a)$, and one can expect better convergence for shifted expansion. The results for the same (6, 0, 0) state are presented below. We used Padé approximants for summation of the residual series $\widetilde{E}_2(D+a)^{-4} + \widetilde{E}_3(D+a)^{-5} + ...$ $(a + a)^{-4} + \widetilde{E}_3(D + a)^{-5} + \dots$

Note the considerable improvement of the convergence in lower orders. Here, the shift parameter is $a = 13.77 + 3.70i$ that is close to $a = 11$ under the previous choice.

More extensive Table 2 compares the unshifted results with the results of these choices of the shift parameter ($a = 2n_1 - 1$ and $a = -E_1/(2E_0)$) for various $(n_1, 0, 0)$ states of helium. We tried another shift parameters for (6, 0, 0) state of helium, see Table 1. Generally, the convergence is weakly dependent on the shift parameter unless it is sufficiently small, $|a| < 10$. Convergence of Padé approximants for unshifted and shifted expansions for the states $(3,0,1)$ and $(6,1,0)$ of helium together with states of the positive ion of lithium is shown in Table 4.

Another summation methods were tried also. For instance, we summed the series for Re *E* and

 $(\text{Im} E)^2$ separately, to eliminate possible square-root singularity at the point where the functions *E* and E^* meet. We tried to sum the series for the function $(E)^{1/2}$ and then to square the result to obtain the energy itself. We tried to choose the shift parameter by more sophisticated method, so that approximants of neighbor orders were equal (by solving a non-linear equation). None of these methods gives remarkable improvement of the convergence.

Real part of the scaled energy $D^2 E$ as a function of $\delta = 1/D$ is shown on Figure 1. For each state, we draw three curves obtained by summation of 13, 14, and 15 terms of the series with the shift parameter $a = 2n_1 - 1$ using Padé approximants. In most cases (except (1,0,0) and (2,0,0) states) all three curves coincide within the accuracy of the plot. The enlarged part of this graph near $D = 3$ is shown on Figure 2. Note that our results always lye slightly up to the results of exact quantum calculations (shown by circles on the figure). The corresponding graphs for the imaginary part are shown on Figure 3. For states $(0,0,0)$ and $(1,0,0)$ it is relatively large even at $D=3$, and so these states cannot be considered as quasistationary. For most of the states, the curves intersect the horizontal axis, and we obtain a meaningless result: $-D^2$ Im $E < 0$. In fact, Im E becomes very small with increasing of $1/D$, but it is still negative. This fault may be a result of insufficient convergence of Padé approximants.

The similar curves for the energy of Li^+ ion are shown on Figures 6 and 7. Curves for the real part are qualitatively similar to helium. The imaginary part remains appreciable at $D = 3$ for $(0, 0, 0)$, $(1, 0, 0)$, and $(2, 0, 0)$ states that appear to be not long-living quasistationary states. In contrast, the helium (2, 0, 0) state is long-living that reflects increasing of stability of such states with decreasing of the nuclear charge (or relative increasing of the repulsion between electrons).

A pattern of poles of Padé approximants for $1/(D+11)$ expansion of the energy for $(6, 0, 0)$ state is shown on Figure 8. Accumulation of poles near the origin reflects an essential singularity at the origin that leads to factorial divergence of the series. A pattern of PA poles for the Borel transform of that series is shown on Figure 9. The poles lying on a positive half-plane may affect the Borel integral and may hinder the convergence of Padé - Borel sums. The same pattern for the "ground" $(0, 0, 0)$ state is shown on Figure 10.

Details of computations

Calculation of coefficients of $1/(D+a)$ -expansion was done using old program with changing the type of all variables to *complex*32* (this program was used in 1983 - 1988 for calculation of ordinary expansion around the real minimum for three-body systems). A text of the full program is printed in Table 3. Calculation of 15 coefficients on *SP2* computer takes 4 - 8 hours for $n_1 = 0$ - 15. Calculation of 19 coefficients for (6,0,0) state needs 26 hours. Changing *complex*32* to *complex*16* slightly speeds up calculations (about 30%). Results of calculations are stored in files *he.dat* and *li.dat* for helium and $Li⁺$ correspondingly. Working directory on personal computer is: *c:\sergeev\ou\fortran\helium\summat*. When this computer is on, it is possible to use *ftp alexei* with *user: dunn* and *password: 455386* to transfer the files. These files are organized as several two-line entries. Each entry corresponds to one state. The first line in each entry is five integers: n_1 , n_2 , n_3 , N , *a* which may follow by a comment. n_1 , n_2 , n_3 are quantum numbers, N is the number of expansion coefficients (including zero-order term), and *a* is the shift parameter. The second line is a list of shifted-expansion coefficients in the form: $(Re \tilde{E}_0, Im \tilde{E}_0)$ $(Re \tilde{E}_1, Im \tilde{E}_1) ... (Re \tilde{E}_{N-1}, Im \tilde{E}_{N-1}).$

We used several tests to evaluate the accuracy of obtained results. Table 5 compares the accuracy of the equilibrium distances and frequencies with the exact results of independent calculations by *Mathematica*. The accuracy appears to be 31 - 32 digits that approaches the limit about 33 digits for *complex*32* arithmetic. Note that these quantities were obtained by numerical iterations since there are no exact analytic formulas for them. The succeeding calculations of coefficients are "exact" in a sense that they are obtained by recurrence relations that contain only four arithmetic operations. Table 6 shows the accuracy of the coefficients calculated by the same program but for the symmetric minimum by comparison with the results of D. Goodson that appear to be slightly more accurate. The accuracy decreases by 1 - 2 digits with increasing of the order by one. The accuracy of the twelfth coefficient E_{11} is 14 digits. Table 7 shows the evaluated accuracy for coefficients for (6,0,0) state of helium. In the first line of each entry, we give the coefficient of the shifted expansion that was calculated directly. In the second line, we give the coefficient of the shifted expansion, that was obtained by re-expansion in powers of $1/(D+a)$ of the unshifted expansion. The accuracy of the last fifteenth coefficient is still sufficiently large, 15 digits in the real part and 14 digits in the imaginary part.

Large- n_1 limit of the dimensional perturbation theory

(Latest note: Similar approach was used for the cubic anharmonic oscillator by G. Alvarez [J. Phys. A: Math. Gen. **22** (1989) 617].)

Existence of long-living asymmetric-configuration states is restricted to relatively large quantum numbers n_1 that was proved by K. Richter et al. within the adiabatic approximation. It is a reason why the behavior at large n_1 may be of interest. Figure 5 shows the behavior of the scaled energy D^2E (real part) as a function of a variable n_1/D . Rapid convergence to some large- n_1 curve is evident, so the energy for sufficiently large n_1 is actually dependent only on one variable $\delta' = n_1 / D$, not on both n_1 and *D*. To prove it, let us consider terms in the large-dimensional expansion (1) separately. The zero-order term in (1) E_0 is a constant (independent on n_1 and *D*). Taking into account Eq. (2), the first order term is $E_1 = \omega_1 \delta' + (\frac{1}{2} \omega_1 + (n_2 + \frac{1}{2}) \omega_2 + (n_3 + \frac{1}{2}) \omega_3 + 6E_0) n_1^{-1}$ that tends to $\omega_1 \delta'$ for large n_1 . Taking into account that E_2 represents the second order polynomial on n_1 of the form $An_1^2 + Bn_1 + C$ (that can be proved by direct computation of this coefficient by recurrence relations), the second order term can be rewritten as $E_2 \delta^2 = A \delta'^2 + B \delta'^2 n_1^{-1} + C \delta'^2 n$ 1 $1 \cdot C\left(\frac{2}{2} \right)$ $\delta^2 = A \delta'^2 + B \delta'^2 n_1^{-1} + C \delta'^2 n_1^{-2}$. It tends to $A \delta'^2$ for large n_1 . By the similar way it can be proved that higher order coefficients also depend only on δ' for large *n*₁. So, the scaled energy D^2E for large *n*₁ tends to some universal function of δ' having the expansion $E'_0 + E'_1 \delta' + E'_2 \delta'^2 + ...$ where $E'_0 = E_0$, $E'_1 = \omega_1$, and generally, E'_k is the coefficient of the highest order term in a polynomial in n_1 that represents E_k as a function of n_1 , e. g. $E_k(n_1) = E'_k n_1^k + E''_k n$ $(n_1) = E'_k n_1^k + E''_k n_1^{k-1} + ...$

The first fifteen coefficients E'_{k} for helium are:

```
(-10.616335150897767811048806451165390,-2.1168970180451802608692347976633732)
(47.167275800327548591182958776531,22.992653433661030887319266650926)
(-181.16083930709028054148349192092,-166.32918653020802428122746979220)
(910.47835748222447613002314893,1084.608492268366961143569468325)
(-6439.539552876040031030774630,-6861.4263564574395384231722209)
(51417.358465983145089021249,41936.570169344947308605728)
(-401412.1572063741976799081,-237732.56700876574043160946)
(2917088.8283426015910588,1111518.3447382370811938)
(-18977650.3874052748593,-2266651.03219716373225)
(101653914.281786512013245,-34778874.9341461271)
(-339365637.62660229,644954506.68744756)
(-839913420.06180,-7201745316.291075)
(26200059441.26,66097521553.27)
(-274286308525.0,-549837050924.0)
(2348865212000.0,4256504929000.0)
```
(the last 1 - 3 significant digits of these numbers may be incorrect because of round-off errors).

A "root test" of the convergence of this series gives convergent numbers:

So, the quasiclassical large- n_1 series has a finite radius of convergence ≈ 0.124 and it has no singularity at the origin unlike an exact finite- n_1 series. It considerably simplifies summation of the series and allows one to sum it even at infinitely large parameter δ' (see the results of summation below).

Figure 4 shows the poles of Padé approximants on the complex plane for the square root of quasiclassical series. The poles does not concentrate near the origin which confirms that the series has a finite radius of convergence. There is a clear accumulation of poles near the point $-0.125 - 0.040i$ that may reflect existence of a singularity here.

Let us consider a "quasiclassical" energy

$$
E' = \lim_{\substack{n_1 \to \infty \\ n_1/D = \text{const}}} n_1^2 E \tag{5}
$$

We proved above that it depends only on one variable $\delta' = n/ D$ and has an expansion

$$
E'(\delta') = E'_0 \delta'^2 + E'_1 \delta'^3 + E'_2 \delta'^4 + \dots \tag{6}
$$

(Latest note: Known as the "classical Birkhoff series", see [Alvarez].)

For large n_1 , the energy may be approximated by Rydberg-like formula having this universal function in the nominator:

$$
E \approx E'(\delta') / n_1^2 \tag{7}
$$

The following table gives the results obtained by the formula (7) in comparison with the exact results for three-dimensional case for $(n_1, 0, 0)$ states,

where the series (6) was summed using Padé approximants. The correction to (7) of the form $E''(\delta') / n_1^3$ may improve the accuracy, but it is beyond our study.

According to the quasiclassical result of K. Richter et al., for large n_1 and $D=3$ the quantity $n_1 \sqrt{-E}$ tends to $S^{\text{sc}} = 1.49150$, the action of the periodic orbit. Within our approach, this quantity equals to the sum of the series $S(\delta') = \delta' \sqrt{-E'_0 - E'_1} \delta' - E'_2 \delta'^2 + ...$ at $\delta' = n_1 / D \rightarrow \infty$. Results of summation at $\delta' = \infty$ are given in the following table. For instance, Padé approximant [1/1] is $-E_0' \delta'$ $-\frac{E_1'}{2E_0'}\delta'$ *E E E* 0 1 1 2 δ δ . It tends to a finite limit $2(-E_0)^{3/2}/\omega_1$ at infinity.

 $\mathbf{0}$

Padé approximant	$S(\infty)$
$\lceil 1/1 \rceil$	$1.34 - 0.21i$
$\lceil 2/2 \rceil$	$1.50 - 0.09 i$
$\left[3/3\right]$	$1.47 - 0.06 i$
[4/4]	$1.47 - 0.06 i$
$\left[5/5\right]$	$1.50 - 0.02 i$
[6/6]	$1.43 + 0.04 i$
7/7 I	$1.45 + 0.02 i$

Padé approximants seem to converge to $1.47 \pm 0.04 + (0.01 \pm 0.03)i$ in agreement with the semiclassical result of K. Richter et al. (1.491...).