Appendix A

Semiclassical case of helium at double-ionization threshold

In the following it will be shortly discussed why quantum chaos is expected close to the double-ionization threshold of helium. For this we will consider the Hamiltonian of classical helium, which can be can read as

$$H = \frac{\mathbf{p}_1^2 + \mathbf{p}_2^2}{2} - \frac{2}{\mathbf{r}_1} - \frac{2}{\mathbf{r}_2} + \frac{1}{\mathbf{r}_1 + \mathbf{r}_2} = E, \tag{A.1}$$

where E is the total energy relative to the double-ionization threshold. If E is positive both electrons can escape, which corresponds to the double-ionization of helium. The region $E < 0$ is more interesting since it represents the region of the doubly excited states. Taking negative energies E into account, one can scale the coordinates as

$$\mathbf{r}_i = \frac{\tilde{\mathbf{r}}_i}{-E} \qquad \mathbf{p}_i = \sqrt{-E}\tilde{\mathbf{p}}_i,$$

and then, the Hamiltonian of classical helium becomes

$$H = \frac{\tilde{\mathbf{p}}_1^2 + \tilde{\mathbf{p}}_2^2}{2} - \frac{2}{\tilde{\mathbf{r}}_1} - \frac{2}{\tilde{\mathbf{r}}_2} + \frac{1}{\tilde{\mathbf{r}}_1 + \tilde{\mathbf{r}}_2} = -1. \tag{A.2}$$

This transformation shows that the dynamics of classical helium remains invariant under variations of the energy since (A.2) can always be obtained by a simple scaling transformation. Under the scaling, the uncertainty principle can be given by

$$\tilde{\hbar} = \Delta\tilde{\mathbf{r}}_i \cdot \Delta\tilde{\mathbf{p}}_i = (-E)\mathbf{r}_i \cdot \frac{\mathbf{p}_i}{\sqrt{-E}} = \sqrt{-E}\hbar. \tag{A.3}$$

As can be seen from (A.3), Planck constant in the rescaled coordinates, $\tilde{\hbar}$, approaches zero as $E \to 0$. Therefore, according to Bohr's correspondence, in the region close to the double-ionization threshold, helium can be described as a semiclassical way where quantum chaos is expected because of the non-integrability in classical helium.

Appendix B

Random matrix theory

Random matrix theory [64, 65], developed in the nineteen fifties and sixties, is a quite successful tool to study the level fluctuations in the quantum spectra of a chaotic system. In this theory, the quantum chaos is accounted for by representing the Hamiltonian by a matrix whose elements are randomly chosen; this represents the minimum knowledge about the system. The construction of a Gaussian ensembles will be illustrated by considering real symmetric 2×2 matrices with $O(2)$ symmetry as their group of orthogonal transformations. What we are seeking is a probability density $P(H)$ of three independent matrix elements H_{11}, H_{22} and H_{12} under the normalization condition

$$\int_{+\infty}^{-\infty} P(H) dH_{11} dH_{22} dH_{12} = 1. \tag{B.1}$$

Two requirements, which take into account very principal physical ideas, suffice to determine $P(H)$. First, $P(H)$ must be invariant under the orthogonal transformation of the two-dimensional basis, i.e.

$$P(H) = P(H'), \quad H' = OHO^T. \tag{B.2}$$

Second, the three independent matrix elements must be uncorrelated. The probability density $P(H)$ must therefore be the product of the three densities,

$$P(H) = P_{11}(H_{11}) P_{22}(H_{22}) P_{12}(H_{12}). \tag{B.3}$$

This assumption can be interpreted as one of minimum-knowledge input or of maximum disorder. The transformation matrix $O(2)$ can be written by

$$O = \begin{pmatrix} cos\Theta & -sin\Theta \\ sin\Theta & cos\Theta \end{pmatrix}. \tag{B.4}$$

One can consider an infinitesimal ($\Theta \to 0$) orthogonal transformation of the basis, and obtains

$$O = \begin{pmatrix} 1 & -\Theta \\ \Theta & 1 \end{pmatrix}. \tag{B.5}$$

Considering $H' = OHO^T$, the matrix elements result in

$$\begin{aligned} H'_{11} &= H_{11} - 2\Theta H_{12} \\ H'_{22} &= H_{22} + 2\Theta H_{12} \\ H'_{12} &= H_{12} + \Theta(H_{11} - H_{22}). \end{aligned} \tag{B.6}$$

According to the invariance given in Eq. (B.2), the factorization and the invariance of $P(H)$ yield

$$P(H) = P(H)\left\{1 - \Theta\left[2H_{12}\frac{d\,lnP_{11}}{dH_{11}} - 2H_{12}\frac{d\,lnP_{22}}{dH_{22}} - (H_{11} - H_{22})\frac{d\,lnP_{12}}{dH_{12}}\right]\right\}. \tag{B.7}$$

Since the infinitesimal angle Θ is arbitrary, its coefficient in Eq. (B.7) should vanish, i.e.

$$\frac{1}{H_{12}}\frac{d\,lnP_{12}}{dH_{12}} - \frac{2}{H_{11} - H_{22}}\left(\frac{d\,lnP_{11}}{dH_{11}} - \frac{d\,lnP_{22}}{dH_{22}}\right) = 0 \tag{B.8}$$

The solution of this equation is given by Gaussian function of the form

$$P(H) = Cexp[-A(H_{11}^2 + H_{22}^2 + 2H_{12}^2) - B(H_{11} + H_{22})]. \tag{B.9}$$

B vanishes if the average energy, $Tr(H)$, is properly shifted to zero, A fixes the unit of energy, and C is determined by the normalization. Without the loss of generality, $P(H)$ can be written as

$$P(H) = Cexp[-A\,TrH^2]. \tag{B.10}$$

It can be shown the probability density (Eq. (B.10)) obtained from the 2×2 matrices in fact holds also for $M \times M$ matrices with arbitrary size.

By assuming that Hamiltonian matrix elements are described according to Eq. (B.10) the eigenvalues are given by

$$E_{\pm} = \frac{1}{2}(H_{11} + H_{22}) \pm \frac{1}{2}\left[(H_{11} - H_{22})^2 + 4H_{12}\right]^{1/2}. \tag{B.11}$$

With the help of the eigenvalues $E_{\pm}$, we obtain the diagonal matrix

$$D = \begin{pmatrix} E_+ & 0 \\ 0 & E_- \end{pmatrix}, \tag{B.12}$$

and by an orthogonal transformation given by Eq. (B.4), one can write the matrix H as

$$H = ODO^T. \tag{B.13}$$

This yields the following transformation between the elements H_{11}, H_{22}, H_{12} and the variables E_+, E_-, Θ:

$$\begin{aligned} H_{11} &= E_+cos^2(\Theta) + E_-sin^2(\Theta), \\ H_{22} &= E_-cos^2(\Theta) + E_+sin^2(\Theta), \\ H_{12} &= (E_+ - E_-)cos\Theta sin\Theta. \end{aligned} \tag{B.14}$$

The Jacobian determinant of this orthogonal transformation is given by,

$$\det(J) = \det\frac{\partial(H_{11}, H_{22}, H_{12})}{\partial(E_+, E_-, \Theta)} = E_+ - E_-. \tag{B.15}$$

Because of

$$P(E_+, E_-, \Theta) = P(H)\det(J) \tag{B.16}$$

and

$$\mathrm{Tr}H^2 = E_+^2 + E_-^2, \tag{B.17}$$

one obtain the distribution $P(E_+, E_-, \Theta)$ in the form:

$$P(E_+, E_-) = C \mid E_+ - E_- \mid exp[-A(E_+^2 + E_-^2)]. \tag{B.18}$$

Note that this form is independent of Θ. To calculate the distribution of nearest-neighbor-spacing (NNS), we should integrate the variables E_+ and E_- in the equation (B.18)

$$P(E_+, E_)= C \int dE_+ \int dE_- \delta(S - \mid E_+ - E_- \mid) \mid E_+ - E_- \mid exp[-A(E_+^2 + E_-^2)]. \tag{B.19}$$

Setting the variables $S = E_+ - E_-$ and the variable $z = (E_+ + E_-)/2$, Eq. (B.19) can be written as

$$\begin{aligned} P(S) &= C' \int_{-\infty}^{\infty} dzS\, exp[-A(S^2/2 + 2z^2)] \\ &= C' \sqrt{\frac{\pi}{2A}} S\, exp(-AS^2/2). \end{aligned} \tag{B.20}$$

A and C' can be evaluated by the normalization condition

$$\int_0^{\infty} dS\, P(S) = 1 \tag{B.21}$$

and with the unit of energy set such that the mean spacing is unity, namely

$$\int_0^{\infty} dS\, S\, P(S) = 1. \tag{B.22}$$

In the end, eq. (B.20) yields the Wigner distribution $P_W(S)$ given in Eq. (4.1)

$$P_W(S) = \frac{\pi}{2} S\, exp(-\frac{\pi}{4} S^2). \tag{B.23}$$