CALCULATION OF THE GROUND ENERGY LEVEL OF HELIUM BY MEANS OF PATH INTEGRALS

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Abstract

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CALCULATION OF THE GROUND ENERGY LEVEL OF HELIUM BY MEANS OF PATH INTEGRALS

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The Feynman formulation of quantum mechanics [(1)] makes it possible to approach the problem of solving quantum-mechanical problems numerically in a rather simple way. The probability amplitude for the transition of a system from point a of configuration space to point b in time t

$$K(b,t;a,0)=\int_a^b \exp\left(\frac{i}{\hbar}S\right)Dx(t) \tag{1}$$

is called the path integral and is the Green' s function of the nonstationary Schrödinger equation. In this case

$$K(b,t;a,0)=\sum \varphi_n(b)\varphi_n^*(a)\exp\left(-\frac{i}{\hbar}E_n t\right) \tag{2}$$

for $t>0$, where φ_n are eigenfunctions, and E_n are eigenvalues of the energy operator. In the general sum (2), one can separate symmetric and antisymmetric terms by taking into account the interchange of electrons at the final point of the trajectory. For symmetric states it is necessary to add amplitudes, and for antisymmetric states to subtract them. Adding a function of the spin coordinates, which is not a solution of the Schrödinger equation, makes it possible to characterize the states in accordance with the Pauli principle. However, this procedure is not necessary when calculating the complete energy spectrum, since the function of the spin coordinates changes not the energy value, but only the amplitude in the sum (2).

If the trajectories of the system are specified approximately in the form of broken lines, then the path integral can be defined as a Riemann integral and, consequently, can be calculated numerically for any system. The real and imaginary parts of the integral, in accordance with (2), are sums:

$$\operatorname{Re} K = \sum A_n \cos \omega_n t; \qquad \operatorname{Im} K = \sum A_n \sin \omega_n t,$$

where $\omega_n = E_n/\hbar$. To find the energy spectrum of a quantum-mechanical system, it is necessary to calculate the integral (1) and, by means of a Fourier transform, find the spectrum $F(\omega)$. Performing such a calculation for the helium atom—a system consisting of a nucleus and two electrons—is of fundamental importance, since helium is the first representative of systems of many particles. Therefore, for characterizing the proposed approximate method it is more important to show its applicability to the helium atom than to the hydrogen atom, although the solution of simpler problems is the classical way of testing any new method.

The classical action S, entering into expression (1), is decomposed into a sum of elementary actions S_j in accordance with the number of segments of the broken line—the trajectory n, i.e., in accordance with the number of time intervals into which the whole time interval t is divided. If the coord-

coordinates and time in reduced units, i.e., introduce $\sigma = \dfrac{t}{n}\dfrac{e^2}{a\hbar}$, $\xi_i = \dfrac{x_i}{a}$, where $a = \hbar^2/me^2$ is the radius of the first Bohr orbit, then the elementary action on a segment of the trajectory approximated by a straight line is expressed for the helium atom by the formula

$$S_j = \hbar \left[\frac{1}{2\sigma} \left(\frac{M_{\text{n}}}{m} \sum_{i=1}^{3} \Delta\xi_i^2 + \sum_{i=1}^{3} \Delta\xi_{1i}^2 + \sum_{i=1}^{3} \Delta\xi_{2i}^2 \right) + \frac{2\sigma}{\xi_1} + \frac{2\sigma}{\xi_2} - \frac{\sigma}{\xi_{12}} \right]; \quad (3)$$

ξ_i, ξ_{1i}, ξ_{2i} are the coordinates of the nucleus, the first and second electrons; ξ_l, ξ_{12} are the distances between the l-th electron and the nucleus and between the electrons. These distances are calculated by interpolation

$$\xi_{lj} = \frac{1}{2}(\xi_{l,j} - \xi_{,j} + \xi_{l,j-1} - \xi_{,j-1}),$$

where j is the number of the segment on the time axis.

If for the electrons the origin of coordinates is taken at the nucleus, and the action associated with the motion of the nucleus is taken outside the integral sign in (1), then it will be necessary to calculate only the integral for the electronic system in the field of the nucleus. It is more convenient to calculate the integral over trajectories with an arbitrary end point and with the initial point at the center of coordinates:

$$L(0,t) = \int_{-\infty}^{\infty} K\, dr_{1b}\, dr_{2b} = \left(\frac{1}{2\pi i\sigma}\right)^{6n/2} \int \cdots \int \exp\left(\frac{i}{\hbar}\sum S_j\right) d\xi_1 \cdots d\xi_{6n} =$$

$$= \sum \left[\int \varphi_n(r_{1b}, r_{2b})\, dr_{1b}\, dr_{2b} \right] \varphi_n^*(0,0) \exp\left(-\frac{i}{\hbar} E_n t\right). \tag{4}$$

In the new variables $\eta_i = \Delta\xi_i/\sqrt{\sigma}$ the value of the integral will not change, while the action element is written more simply:

$$S_{j\,\mathrm{el}} = \hbar \left\{ \sum_{i=1}^{6} \frac{\eta_{ij}^2}{2} + \left(\frac{2}{\beta_{1j}} + \frac{2}{\beta_{2j}} - \frac{1}{\beta_{12j}} \right) \sqrt{\sigma} \right\},$$

$$\beta_l = \frac{1}{2} \left[\sum_{i=1}^{3} \left(\sum_{k=1}^{j} \eta_{ikl} + \sum_{k=1}^{j-1} \eta_{ikl} \right)^2 \right]^{1/2},$$

$$\beta_{12} = \frac{1}{2} \left[\sum_{i=1}^{3} \left\{ \left(\sum_{k=1}^{j} \eta_{ik1} + \sum_{k=1}^{j-1} \eta_{ik1} \right) - \left(\sum_{k=1}^{j} \eta_{ik2} + \sum_{k=1}^{j-1} \eta_{ik2} \right) \right\}^2 \right]^{1/2}. \tag{5}$$

The practical calculation of integral (4) must be carried out over a corridor of trajectories with the maximum segment value along each coordinate a. For the last segment this value must be increased several times in order to ensure a more uniform distribution of the end points over the volume. The integral of finite multiplicity is calculated as

$$L = \frac{1}{(2\pi i)^{6n/2}} \int_{-a}^{+a} \cdots \int_{-a}^{+a} \exp\left(i \sum S_j\right)\, d\eta_1\, d\eta_2 \cdots d\eta_{6n}. \tag{6}$$

Such an estimate of integral (4) is possible because trajectories with a large value of the action, i.e. mostly long trajectories, make a small contribution to the integral because of the rapid oscillation of the phase $\exp(iS)$. Integral (6) was calculated by the Monte Carlo method using the formula

$$L = \frac{1}{N} \left(\frac{2a}{\sqrt{2\pi i}} \right)^{6n} \sum_{k=1}^{N} \left\{ \exp\left(i \sum S_j\right) \right\}_k, \tag{7}$$

where N is the number of trajectories with the specified maximum step over the time σ. The segment of the trajectory at the j-th step was estimated with the aid of random numbers α_j: $\eta_{ij} = a\alpha_j$, where α_j is uniformly distributed in the interval $[-1; +1]$. The aperiodicity interval used to calculate the sequence

random numbers is about 400,000. Therefore $n = 40$ was chosen, so that, with a sufficient number of trajectories, the total number of random numbers would not exceed the aperiodicity interval. The form of the curve after calculation of

1800 trajectories is shown in Fig. 1, where $\mathrm{Re}\, L(t)$ is given at 250 points with interval $\Delta t = 0.1$ in the adopted units.

The method of estimating integral (4) by selecting a corridor of trajectories is sufficiently accurate only as $\sigma \to 0$, i.e., in the case of an infinite integral.

Fig. 1 Fig. 2

Fig. 1. Real part of the integral over trajectories as a function of time after 1800 trajectories

Fig. 2. Energy spectrum of the helium atom

In the case of an integral of finite multiplicity, it is necessary to reduce the error at large t by decreasing the contribution of points at large t in the Fourier transform. It is convenient to use for this the formula:

$$F(\omega) = \int_{-\infty}^{+\infty} \mathrm{Re}\, L(t) \exp(-pt^2) \cos \omega t \, dt =$$

$$= \sum_n \frac{1}{4} \left(\frac{\pi}{p}\right)^{1/2} \left\{ \exp\left[-\frac{(\omega - \omega_n)^2}{4p}\right] + \exp\left[-\frac{(\omega + \omega_n)^2}{4p}\right] \right\}, \qquad (8)$$

where ω_n is the frequency corresponding to the energy level of the given system. We applied formula (8) to calculate the spectrum shown in Fig. 2 with $p = 0.0006$, which gave a spectrum with broad maxima. The leftmost maximum corresponds to the ground level of helium $\omega_0 = 2.92 \pm 0.05$ atomic units, which differs from the experimental value 2.90351 by 0.57%. The levels of the excited helium atom did not appear in the spectrum because of the small value of $\varphi_n(0)$ for these levels and, correspondingly, the large width of the main maximum. As for the two maxima $\omega = 1.65$ and $\omega = 0.90$, they may be interpreted as x-ray terms of the helium atom or energy levels of the helium ion. It should be noted, however, that the Fourier transform (8) was carried out over a comparatively small interval of t. Therefore the low frequencies in the energy spectrum are determined with a significantly larger error than the ground level. The calculations were performed on the "Nairi" computer at a speed of 100 operations/sec. The use of machines with higher speed and a more perfect random-number generator will possibly lead to improvement of the results, as is confirmed by the following data:

Number of trajectories	900	1200	1500	1800
ω_0	3.15	3.20	2.95	3.92

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1. R. Feynman, A. Hibbs, *Quantum Mechanics and Path Integrals*, Moscow, 1968.

Note: Figure translations are in progress. See original paper for figures.