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Moment distributions of clusters and molecules in the adiabatic rotor model ☆

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Abstract

We present a Fortran program to compute the distribution of dipole moments of free particles for use in analyzing molecular beams experiments that measure moments by deflection in an inhomogeneous field. The theory is the same for magnetic and electric dipole moments, and is based on a thermal ensemble of classical particles that are free to rotate and that have moment vectors aligned along a principal axis of rotation. The theory has two parameters, the ratio of the magnetic (or electric) dipole energy to the thermal energy, and the ratio of moments of inertia of the rotor.

Program summary

Program title: AdiabaticRotor
Catalogue identifier: ADZO_v1_0
Program summary URL: http://cpc.cs.qub.ac.uk/summaries/ADZO_v1_0.html
Program obtainable from: CPC Program Library, Queen's University, Belfast, N. Ireland
Licensing provisions: Standard CPC licence, http://cpc.cs.qub.ac.uk/licence/licence.html
No. of lines in distributed program, including test data, etc.: 479
No. of bytes in distributed program, including test data, etc.: 4853
Distribution format: tar.gz
Programming language: Fortran 90
Computer: Pentium-IV, Macintosh Power PC G4
Operating system: Linux, Mac OS X
RAM: 600 Kbytes
Word size: 64 bits
Classification: 2.3
Nature of problem: The system considered is a thermal ensemble of rotors having a magnetic or electric moment aligned along one of the principal axes. The ensemble is placed in an external field which is turned on adiabatically. The problem is to find the distribution of moments in the presence of the external field.
Solution method: There are three adiabatic invariants. The only nontrivial one is the action associated with the polar angle of the rotor axis with respect to external field. It is found by Newton's method.
Running time: 3 min on a 3 GHz Pentium IV processor.
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☆ This paper and its associated computer program are available via the Computer Physics Communications homepage on ScienceDirect (http://www.sciencedirect.com/science/journal/00104655).

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Keywords: Molecular spectra; Dipole moments; Atomic clusters

1. Introduction

It is common to measure the magnetic moment or the electric dipole moment of clusters or small molecules by the deflection of a molecular beam by an inhomogeneous field [1–6]. These experiments take place in the gas phase using Stern–Gerlach magnets to deflect the beam in the magnetic case [5,6] and using an electric field gradient in the electric case [1–4]. One needs a theory of the moment distribution to relate the observed deflections to the intrinsic moment of the particles. There are two well-known limits for the distribution, the quantum limit of a spin with a fixed total angular momentum, and superparamagnetic limit, where the moments are thermally distributed. Neither of these limits is valid for the typical situation of a nanoparticle, which may have a moment with fixed orientation in a body-centered frame, but changing orientation in the laboratory frame. If we assume that an external field is introduced adiabatically, the distribution of moments can be computed using the adiabatic invariants of the rigid rotor. This classical theory and a method of solution was given in Refs. [7–9]. While conceptually the theory is quite straightforward, the computation is not completely trivial. We first present the equations that govern the deflections, and then the computational aspects [10].

2. Theory

We consider a ferromagnetic particle having a magnetic moment aligned along the 3-axis and equal moments of inertia around the 1 and 2 axes in the body-fixed frame. Its Lagrangian is given by

$$L = \frac{J_1}{2}(\dot\theta^2 + \dot\phi^2 \sin^2\theta) + \frac{J_3}{2}(\dot\psi + \dot\phi\cos\theta)^2 + \mu_0 B\cos\theta, \tag{1}$$

where J_1, $J_2 = J_1$ and J_3 are the principal moments of inertia and θ, ϕ, ψ are the Eulerian angles of the 3-axis with respect to the magnetic field B. The theory would be the same for a particle with an intrinsic electric dipole moment p_0 in an electric field E, simply replacing $\mu_0 B$ by $p_0 E$ in all equations. There are three constants of motion for the Lagrangian equation (1). They are the energy E,

$$E = \frac{J_1}{2}(\dot\theta^2 + \dot\phi^2 \sin^2\theta) + \frac{J_3}{2}(\dot\psi + \dot\phi\cos\theta)^2 - \mu_0 B\cos\theta, \tag{2}$$

the angular momentum about the field direction m_z,

$$m_z \equiv \frac{\partial L}{\partial \dot\phi} = J_1\dot\phi\sin^2\theta + J_3(\dot\psi + \dot\phi\cos\theta)\cos\theta, \tag{3}$$

and the angular momentum about the 3-axis m_3,

$$m_3 \equiv \frac{\partial L}{\partial \dot\psi} = J_3(\dot\psi + \dot\phi\cos\theta). \tag{4}$$

The last quantity, m_3, is only conserved because of the condition we imposed that $J_2 = J_1$. Under the equation of motion, the variable θ has a periodic dependence on time, oscillating between two limits θ_1 and θ_2. For convenience below, we replace the variable θ by its cosine, $u = \cos\theta$. The quantity of interest for the deflection measurement is the average moment of the particle $\bar\mu = \mu_0\bar u$ where $\bar u$ is the average of u over a cycle. There is an analytic formula for this quantity in terms of the elliptic integrals $K(\nu)$ and $E(\nu)$ which can be compactly expressed in term of the three zeros u_0, u_1, u_2 of the cubic polynomial

$$f(u) = \big(2J_1E - J_1m_3^2/J_3 + 2J_1\mu_0 Bu\big)(1-u^2) - (m_z - m_3u)^2. \tag{5}$$

The formula for $\bar u$ is [11]

$$\bar u = \frac{u_0K(\nu) + (u_2 - u_0)E(\nu)}{K(\nu)}, \tag{6}$$

where $\nu = (u_2 - u_1)/(u_2 - u_0)$.

We use Eq. (6) to compute $\bar u$ as a function of m_3, m_z and E. However, E changes as the particle enters the field. Assuming the field change is adiabatic, the action J_θ associated with the variable θ remains constant and thus can be used to determine the new value of E. There is no analytic expression for $E(J_\theta)$ or even for the inverse function $J_\theta(E)$. In the program we compute the latter from its definition

$$J_\theta = 2\int_{u_1}^{u_2} \frac{\sqrt{f(u)}}{1-u^2}\,\mathrm{d}u. \tag{7}$$

In zero external field, the action is simply related to the total angular momentum I,

$$I = \max\big(|m_3|, |m_z|\big) + \frac{J_\theta}{2\pi}. \tag{8}$$

This relation is useful to make a connection to the quantum mechanical formulation of the problem as well as to make tests of the program.

The probability distribution $P(u)$ that we seek to compute can now be expressed as the three-dimensional integral,

$$P(u) = \frac{1}{Z(T)}\int_0^\infty \mathrm{d}I \int_{-I}^{I}\mathrm{d}m_z \int_{-I}^{I}\mathrm{d}m_3\,\delta\big(u - \bar u(I, m_z, m_3)\big) \times \exp(-E_0/kT), \tag{9}$$

where the partition function $Z(T)$ is the corresponding integral without the delta function and $E_0 = (I^2 - m_3^2)/2J_1 + m_3^2/2J_3$. There are two symmetries that can be used to reduce the size of the integration region. Namely, $\bar u(I, m_z, m_3)$ remains the same under the interchange of m_z and m_3 and under the replacement $m_3, m_z \to -m_3, -m_z$. While Eq. (9) is expressed in terms of dimensioned physical parameters, in fact the results only depend on two dimensionless combinations of those parameters,

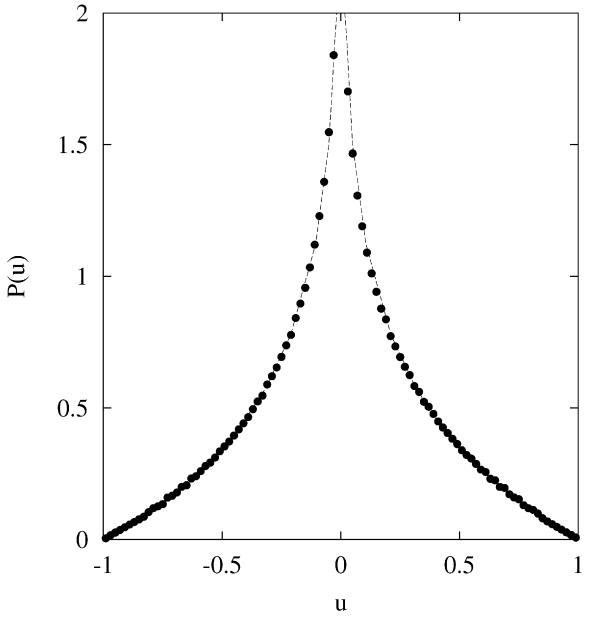

Fig. 1. Zero field distribution compared with the numerical results for $x = 0.01$ and $J_1/J_3 = 1$.

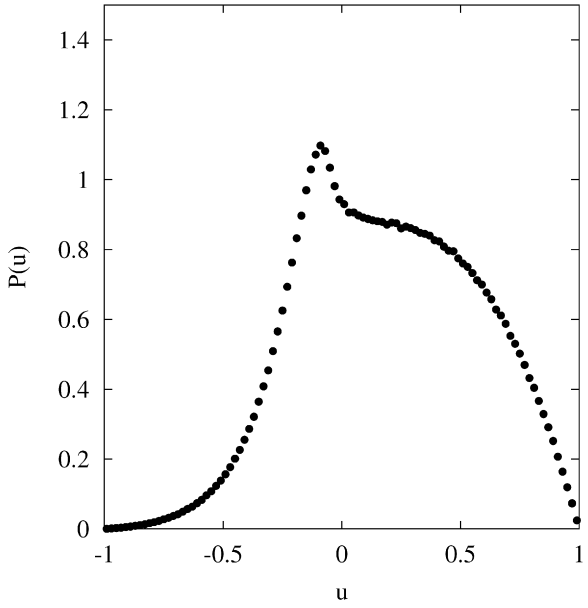

Fig. 2. Distribution $P(u)$ computed for $x = 1$ and $J_1/J_3 = 1$.

namely

$$x = \frac{\mu_0 B}{kT} \tag{10}$$

and J_1/J_3. Note that the distribution function is independent of the overall magnitudes of the moments of inertia.

3. Numerical

We evaluate the integral (9) using uniform meshes in the three integration variables, binning values of $\bar{u}$ on the mesh points to construct the probability density. This requires a fine integration mesh due to the singularities and discontinuities in the integrand. We use a mesh size of $\Delta m/I \approx 0.005$ to achieve an accuracy suitable for graphing the distribution $P(u)$. It also helps to have incommensurate mesh spacings for two m integrations.

Another numerical problem is connected with determining $\bar{u}$ as a function of J_θ. Both quantities are computed directly in terms of the energy variable E, but to find $\bar{u}$ as a function of J_θ requires solving an implicit equation. In the program this is carried out by Newton's method; a warning is given if the convergence is poor.

4. Tests and program use

There are two analytic tests that can be made of the program. The first is the probability distribution at zero field, which is given [9] by

$$P(u) = \frac{1}{2}\log\bigl(1/|u|\bigr). \tag{11}$$

Unfortunately, Eq. (6) cannot be used at $B = 0$ because u_0 goes to infinity at that point. However, the numerical parameters in the program have been set so that the distributions are accurate to within a few percent for values of x greater than 0.01. Fig. 1 show the comparison of Eq. (11) with the computed distribution at $x = 0.1$ with the mesh as given above. The small irregularities are the binning effects associated with the finite mesh size.

The second analytic test is the ensemble-average moment $\langle\bar{u}\rangle$ at small fields. It is given by

$$\langle\bar{u}\rangle \approx \frac{2}{9}x. \tag{12}$$

The computed ensemble average for $x = 0.01$ is $\langle\bar{u}\rangle = 0.000222$, in excellent agreement with Eq. (12).

The program runs without any input file, as all of the parameters have been set in the Fortran coding. The important physical parameters x and J_1/J_3 are specified on lines 22 and 25 of the code, respective. Running the code with the values given,

```
betamu0B=1.0d0
J1J3=1.d0
```

gives as direct output the values of x, J_3/J_1 and $\langle\bar{u}\rangle$,

```
1.000 1.000 0.19220
```

The program also writes a data file 'udist.dat' that has a table of values of u and $P(u)$. Fig. 2 shows a plot of that data.

Acknowledgements

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[10] Program available at: http://gene.phys.washington.edu/~bertsch/adiabatic.f.
[11] We note a typographical error in the formula as presented in Ref. [7], Eq. (2.23) of that reference.