Eur. Phys. J. D **33**, 35–38 (2005)
DOI: 10.1140/epjd/e2005-00027-7

THE EUROPEAN PHYSICAL JOURNAL D

Aharonov-Carmi effect and energy shift of valence electrons in rotating C_{60} molecules

J.Q. Shen[1,2,a], S. He[2], and F. Zhuang[3]

[1] Centre for Optical and Electromagnetic Research, Zhejiang University, Hangzhou Yuquan 310027, P.R. China
[2] Zhejiang Institute of Modern Physics and Department of Physics, Zhejiang University, Hangzhou Yuquan 310027, P.R. China
[3] Institute of Condensed Matter Physics and Department of Physics, College of Science, Hangzhou Teacher's College, Hangzhou 310012, P.R. China

Received 26 October 2004

Abstract. The molecular Aharonov-Carmi (A-C) effect is considered for C_{60} molecules. It is shown that the valence electrons in rapidly rotating C_{60} molecules acquire an A-C phase shift, which is proportional to the molecular angular velocity flux enclosed by the valence-electron matter wave on the C_{60} molecular shell. The energy shift of the valence electrons due to both the molecular rapid rotation and the molecular A-C phase shift is calculated.

PACS. 03.65.Vf Phases: geometric; dynamical or topological – 61.48.+c Fullerenes and fullerene-related materials

1 Introduction

Molecular rotation gives rise to some novel effects such as the quantum decoherence induced by stimulated two-photon Raman processes, the laser-driving rotational transitions [1] and the electron spin-rotation geometric phase shift [2]. According to the principle of equivalence, the molecular rotational dynamics can be treated inside the theoretical framework of weak "gravitational" fields. Thus, one can predict some interesting quantum gravitational (inertial) effects for the rapidly rotating molecules. Such effects may be particularly significant for the molecules in solid, since it may provide us with an insight into the molecular rotational dynamics of condensed phases [3], including the problems of the intermolecular interaction and phase behavior (phase diagram) [3–5]. As to the quantum gravitational (inertial) effects, historically, with the development of laser technology and its application to the gravitational interferometry experiments [6–8], some weak gravitational effects associated with gravitomagnetic fields [9,10] have become increasingly important both theoretically and experimentally, and therefore captured attention of many investigators [11–14]. During the past 20 years, neutron interferometry was developed with an increasing accuracy. For example, by using these technologies, Werner et al. investigated the neutron analog of the Foucault-Michelson-Gale effect in 1979 [11] and Atwood et al. found the neutron Sagnac effect in 1984 [12]. Aharonov, Carmi et al. [13,15] proposed a gravitational analog to the Aharonov-Bohm effect [16–18]. This is a geometric (topological) effect of vector potential of the inertial force field: specifically, in a rotating frame the matter wave propagating along a closed path will acquire a non-integral phase (geometric phase). This phenomenon has now been called the Aharonov-Carmi (A-C) effect, or the gravitational (inertial) Aharonov-Bohm effect. Overhauser, Colella [19], Werner and Standenmann et al. [11] have demonstrated the existence of such a geometric effect by means of the neutron-gravity interferometry experiments. Note that here all these phenomena were found and studied in macroscopic experiments. In the present paper, however, we will consider the molecular A-C effect in rotating C_{60} molecules, where the molecular rotation provides an effective weak "gravitomagnetic" field acting upon the valence electrons.

2 A-C effect of valence electrons

In the literature, the nuclear-magnetic resonance (NMR) studies [20] and the quasi-elastic neutron scattering experiments [21] were performed to obtain the information on the rotational dynamics of C_{60} molecules in solid phases. It was shown by these methods that C_{60} molecules in the orientationally disordered phase experience a rapid rotation, the rotational correlation time of which may be picoseconds. It follows that the molecular dynamics of C_{60} rotation is of particular importance, since it has close relation

---

[a] e-mail: `jqshen@coer.zju.edu.cn`

to the molecular thermal motion, phase transition and crystal structure of C_{60} solid [3–5]. Here, we first consider the molecular A-C effect and A-C phase shift of valence electrons due to the rotational motion of C_{60}.

As for the electronic structure and bonding in C_{60} molecule, the Hückel molecular orbital theory for non-planar conjugated organic molecules has been applied to study the electronic state and properties of the icosahedral geometry of C_{60} [22]. The molecule was calculated to have a stable closed shell singlet ground electronic state. Although there are two independent bond types (i.e., 30 bonds which lie solely in 6-MRs, while 60 bonds form the edges of both a 5- and a 6-MR), the experimental observations showed that the molecule is non-alternant, but that the charge densities are all equal as a result of the symmetry of the molecule itself [22,23]. In order to study the molecular A-C effect in C_{60}, here we consider only the interference behavior of one of the valence electrons (e.g., the delocalized π-bond electrons on shell), which undergo an inertial coupling (i.e., the Coriolis force) to the molecular rotation. The Hamiltonian of the valence electron that is acted upon by a Coriolis force due to the molecular rapid rotation is of the form

$$H(\mathbf{r}) = \frac{1}{2m_{\mathrm{e}}} \left(-i\hbar\nabla - 2m_{\mathrm{e}}\mathbf{a}\right)^2, \tag{1}$$

where m_{e} denotes the electron mass, and the effective gravitomagnetic vector potential $\mathbf{a}$ is so defined that the molecular angular velocity $\vec{\omega} = \nabla \times \mathbf{a}$. In general, $\mathbf{a}$ in a spherical coordinate system (r, θ, φ) can be written as $a_r = 0$, $a_\theta = 0$ and $a_\varphi = (\omega r/2)\sin\theta$. The eigenvalue equation of H is $H(\mathbf{r})\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$. It is apparently seen that the stationary-state wavefunction $\Psi(\mathbf{r})$ of the electron can be rewritten as

$$\Psi(\mathbf{r}) = \exp\left(\frac{i2m_{\mathrm{e}}}{\hbar}\int_{\mathbf{r}_0}^{\mathbf{r}} \mathbf{a}\cdot \mathrm{d}\mathbf{l}\right)\Psi_0(\mathbf{r}), \tag{2}$$

where $\mathbf{r}_0$ denotes the initial position vector of the integral interval. The wavefunction $\Psi_0(\mathbf{r})$ satisfies the stationary equation $-\left(\hbar^2/2m_{\mathrm{e}}\right)\nabla^2\Psi_0(\mathbf{r}) = E\Psi_0(\mathbf{r})$. Thus, the A-C phase shift acquired by the valence electron is $\Delta\phi = (2m_{\mathrm{e}}/\hbar)\oint_{\mathbf{l}} \mathbf{a}\cdot \mathrm{d}\mathbf{l}$, which can be rewritten as

$$\Delta\phi = \frac{2m_{\mathrm{e}}}{\hbar}\oiint_{\mathbf{S}} (\nabla\times\mathbf{a})\cdot \mathrm{d}\mathbf{S} = \frac{2m_{\mathrm{e}}}{\hbar}\vec{\omega}\cdot\mathbf{A} \tag{3}$$

with $\mathbf{A}$ being the area vector circulated by the standing wave of the valence electron on the C_{60} molecular shell (see Fig. 1). Obviously, the expression $\vec{\omega}\cdot\mathbf{A}$ in equation (3) is just the molecular rotational angular velocity flux. According to the principle of equivalence, the Coriolis force acting upon the valence electron can be considered a gravitomagnetic Lorentz force. In this sense, the expression $\vec{\omega}\cdot\mathbf{A}$ can also be referred to as the gravitomagnetic flux enclosed by the valence-electron matter wave. In what follows, we will evaluate the order of magnitude of the A-C phase shift acquired by the electron. In the high-temperature phase (orientationally disordered phase), ω may be 10^{11} rad/s [24]. Thus the order of magnitude of the molecular A-C phase shift in a rotating C_{60} molecule may be 10^{-3}. Here we have taken a typical value 3×10^{-19} m^2 for the modulus of the area vector $\mathbf{A}$. Since it has no connection with the dynamical quantities such as electron energy and velocity, the A-C phase shift $\Delta\phi$ is viewed as a geometric (topological) phase shift [25–29].

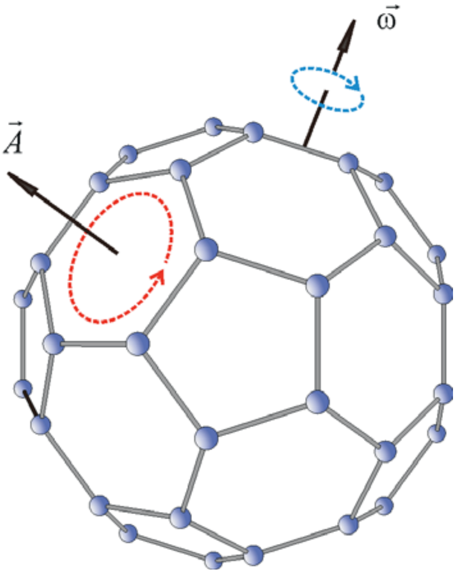

Fig. 1. Schematic diagram for a rotating C_{60} molecule and the valence-electron matter wave on the C_{60} molecular shell. The valence-electron matter wave on the shell will acquire a geometric phase shift and hence an energy shift due to the rapid rotation (e.g., 10^{11} rad/s) of the C_{60} molecule in an orientationally disordered phase.

It should be noted that such an additional phase shift will have influence on the wave interference (to form the standing wave) of valence electrons on the C_{60} molecular spherical shell. As a result, the energy of the valence electrons in C_{60} molecules will inevitably be shifted, which may have an observable effect on the C_{60} photoelectron spectroscopy. In the following, we will discuss such an energy shift resulting from the C_{60} molecular A-C effect.

3 Energy shift due to A-C effect

In the spherical coordinate system, the on-shell wavefunction, $\Psi_0(\mathbf{r})$, of the valence electron can be written in the form $R(r_0)\Theta(\theta)\Phi(\varphi)$, where r_0 denotes the radius of the C_{60} molecule. With the help of the eigenvalue equation of $\Psi_0(\mathbf{r})$, one can arrive at

$$\begin{aligned} &E = \lambda\frac{\hbar^2}{2m_{\mathrm{e}}r_0^2}, \\ &\frac{1}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right) + \left(\lambda - \frac{m^2}{\sin^2\theta}\right)\Theta = 0, \\ &\Phi(\varphi) = \frac{1}{\sqrt{2\pi}}\exp(im\varphi). \end{aligned} \tag{4}$$

Thus, it follows from equations (2) and (4) that the φ-dependent total phase in $\Psi(\mathbf{r})$ is

$$\phi(\varphi) = m\varphi + \frac{2m_{\mathrm{e}}}{\hbar}\int_{\mathbf{r}_0}^{\mathbf{r}} \mathbf{a}\cdot \mathrm{d}\mathbf{l} = m'\varphi \qquad (5)$$

with

$$m' = m + \frac{m_{\mathrm{e}}\omega r_0^2 \sin^2\theta}{\hbar}. \qquad (6)$$

Note that the expressions $a_r = 0$, $a_\theta = 0$ and $a_\varphi = (\omega r/2)\sin\theta$ for the gravitomagnetic vector potential $\mathbf{a}$ have been inserted into the total phase (5). Since the wavefunction has to be a single-valued function of position, m' in equations (5) and (6) must be an integer. This, therefore, implies that m in equations (4) is no longer an integer. Instead, as seen from equation (6), it is a function of θ. Inserting the relation $m = m' - m_{\mathrm{e}}\omega r_0^2 \sin^2\theta/\hbar$ into the second equation of equations (4), one can obtain

$$\frac{1}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right) + \left(\lambda' - \frac{m'^2}{\sin^2\theta}\right)\Theta = 0, \qquad (7)$$

where

$$\lambda' = \lambda + \frac{2m_{\mathrm{e}}m'\omega r_0^2}{\hbar}. \qquad (8)$$

Note that in equation (7), we have ignored the small term $\left(m_{\mathrm{e}}\omega r_0^2/\hbar\right)^2 \sin^2\theta\Theta$, which is about only one part in 10^6 of the retained term $(m'^2/\sin^2\theta)\Theta$. It is clear that the parameter λ' in equation (7) takes $\lambda' = l(l+1)$, where l is the angular quantum number (integer). Thus, it follows from the expression (8) that λ is constant (independent of position θ) but no longer an integer. Substitution of the expression $\lambda = \lambda' - 2m_{\mathrm{e}}m'\omega r_0^2/\hbar$ into the energy eigenvalue E in equations (4), one can arrive at the expression for the energy shift of valence electron, i.e.,

$$\Delta E = -m'\hbar\omega. \qquad (9)$$

This is the energy-shift effect of the valence electron due to the C_{60} molecular rotation (and hence the molecular A-C effect). The physical meanings of (9) can be considered an interaction between the gravitomagnetic moment ($m'\hbar$) and the gravitomagnetic field (ω).

At 283 K it was measured that the C_{60} molecular reorientational correlation time, τ, is 9.1 picoseconds that is three times as long as the calculated correlation time τ ($\equiv (3/5)\,(I/k_B T)^{\frac{1}{2}}$ with k_B and T being Boltzmann's constant and the absolute temperature, respectively) for free rotation (i.e., the unhindered gas-phase rotation) at this temperature [24]. This means that in a high-temperature phase (orientationally disordered phase), the rotating frequency ω may be 10^{11} rad/s. Thus such an energy shift (9) may be of the order of magnitude of $10^{-4} \sim 10^{-3}$ eV in an orientationally disordered phase.

4 Concluding remarks

We considered the A-C effect and energy shift of valence electrons due to the rotational motion of C_{60}. Since C_{60} molecules possess a spherically symmetric geometric shape, it rotates rapidly at about 10^9 rad/s (in the orientationally ordered phase) and at about 10^{11} rad/s (in the orientationally disordered phase) [24]. Moreover, in C_{60} condensed phases the molecule is subject to a fluctuation (precession and nutation) of the rotational motion caused by the non-central intermolecular potential. It can be readily verified that the precessional frequency of C_{60} rotation in the orientationally ordered phase may be very large, e.g., it ranges from 10^{12} to 10^{14} rad/s [2]. Here it is worth noting that even though the molecular precessional frequency is so great, the result of (9) still holds, since the non-central intermolecular potential leads only to the variation of the direction of the angular velocity of rotating C_{60} molecules but the magnitude of angular velocity does not alter much. It is known that the analysis of the intermolecular potential is essential for both the molecular-dynamics (MD) simulation and the study of the high-temperature phase diagram of C_{60} solid [3–5]. So, the treatment of the fluctuation of the molecular rotational motion is also important for considering these subjects. Because the electron spin can be coupled to the molecular angular velocity (spin-rotation coupling) [30], such a significant precession of C_{60} rotation will unavoidably result in a so-called spin-rotation phase shift acquired by the valence electrons [2]. Thus, both the molecular rotation and the precession can yield the valence-electron state plus the geometric phase shifts. We think that the information on these geometric phase shifts (and hence energy shift) may be read off from the photoelectron spectroscopy of C_{60}. For these reasons, the molecular A-C effect, the consequent valence-electron energy shift as well as some properties relevant to the above-mentioned effects (e.g., electron spin-rotation coupling [2]) deserve consideration for the investigation of the molecular rotational dynamics of C_{60} solid.

J.Q. Shen is financed by the Wenner-Gren foundations, Stockholm. S. He is supported by the National Natural Science Foundation of China under Project No. 10074053 and the Zhejiang Provincial Natural Science Foundation under Project No. 100019. F. Zhuang is supported by the Zhejiang Provincial Education Bureau's Education-Research Conveyance Project under Grant No. 2002 ZSMN002.

References

1. A. Adelswärd, S. Wallentowitz, J. Opt. B **6**, S147 (2004)
2. J.Q. Shen, S.L. He, Phys. Rev. B **68**, 195421 (2003)
3. C. Caccamo, Phys. Rev. B **51**, 3387 (1995)
4. V.I. Zubov, J.F. Sanchez-Ortiz, J.N. Teixeira-Rabelo, I.V. Zubov, Phys. Rev. B **55**, 6747 (1997)
5. M. Hasegawa, K. Ohno, J. Chem. Phys. **113**, 4315 (2000)
6. B.J. Ahmedov, Phys. Lett. A **256**, 9 (1999)
7. I. Ciufolini, E. Pavlis, F. Chieppa, Science **279**, 2100 (1998)
8. H. Hayasaka, S. Takeuchi, Phys. Rev. Lett. **63**, 2701 (1989)
9. J.Q. Shen, Phys. Rev. D **70**, 067501 (2004)
10. J.Q. Shen, Ann. Phys. (Leipzig) **13**, 532 (2004)

11. S.A. Werner, J.L. Staudenmann, R. Colella, Phys. Rev. Lett. **42**, 1103 (1979)
12. D.K. Atwood, M.A. Horne, C.G. Shull, J. Arthur, Phys. Rev. Lett. **52**, 1673 (1984)
13. J. Anandan, Phys. Rev. D **15**, 1448 (1977)
14. M. Dresden, C.N. Yang, Phys. Rev. D **20**, 1846 (1979)
15. Y. Aharonov, G. Carmi, Found. Phys. **3**, 493 (1973)
16. Y. Aharonov, D. Bohm, Phys. Rev. **115**, 485 (1959)
17. J. Audretsch, V.D. Skarzhinsky, Phys. Rev. A **60**, 1854 (1999)
18. J.-B. Yau, E.P. De Poortere, M. Shayegan, Phys. Rev. Lett. **88**, 146801 (2002)
19. A.W. Overhauser, R. Colella, Phys. Rev. Lett. **33**, 1237 (1974)
20. C.S. Yannoni et al., J. Phys. Chem. **95**, 9 (1991)
21. D.A. Neumann, J.R.D. Copely, R.L. Cappelletti et al., Phys. Rev. Lett. **67**, 3808 (1991)
22. R.C. Haddon, L.E. Brus, K. Raghavachari, Chem. Phys. Lett. **125**, 459 (1986)
23. R.L. Disch, J.M. Schulman, Chem. Phys. Lett. **125**, 465 (1986)
24. R.D. Johnson et al., Science **255**, 1235 (1992)
25. M.V. Berry, Proc. Roy. Soc. Lond. A **392**, 45 (1984)
26. R.Y. Chiao, Y.S. Wu, Phys. Rev. Lett. **57**, 933 (1986)
27. A. Tomita, R.Y. Chiao, Phys. Rev. Lett. **57**, 937 (1986)
28. J.Q. Shen, H.Y. Zhu, P. Chen, Eur. Phys. J. D **23**, 305 (2003)
29. J.Q. Shen, Eur. Phys. J. D **30**, 259 (2004)
30. B. Mashhoon, Phys. Rev. Lett. **61**, 2639 (1988)