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Discontinuity of dipole-moment matrix elements in ellipsoidally shaped nanoparticles and profiles of spectral lines

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ABSTRACT

The behaviour of energy levels and optical spectra of a charged particle (electron or hole) confined within a potential well of ellipsoidal shape is investigated as a function of the shape-anisotropy parameter. If two energy levels of the same symmetry intersect in a perturbation-theory approximation, they move apart on direct diagonalization of the appropriate Hamiltonian. The intersection of the energy levels leads to a discontinuity of the corresponding dipole-moment matrix element. The discontinuity of matrix elements is not reflected in the behaviour of transition probabilities which are continuous functions of the shape-anisotropy parameter. The profiles of a spectral line emitted or absorbed by an ensemble of ellipsoidally shaped nanoparticles with a Gaussian distribution of size are calculated and discussed.

1. Introduction

In a regime of strong size quantization, the electron-hole Coulomb interaction energy is much less than the energy of a charged-particle electron or hole confined within a crystalline semiconductor structure of varied shape and nanometre size. In this regime one can hence neglect the Coulomb interaction and treat the electron and hole independently. The most important result that early investigations revealed is the strong interdependence between the character of the energy spectrum of the nanometre-size object and its geometrical parameters [1]. In these works, the qualitative and quantitative descriptions of the electronic, optical and mechanical properties apply to spherical nanoparticles, i.e., for spherical quantum dots (see Ref. [2] and references therein). The properties of nanoparticles having cylindrical [3–6], ellipsoidal [7–10], semi-ellipsoidal [11], pyramidal and lens shape with infinite and finite [12–14] barrier heights were subsequently analysed. Furthermore, to facilitate the comparison of calculated results with the probable and available experimental data, size distribution of growing quantum dots have been taken into account [15–18].

Experiments indicate that small nanoparticles have a nearly spherical shape, whereas large nanoparticles have an ellipsoidal shape. For the growth of a nanoparticle with various methods, the energy spectrum varies continuously with its size and shape. An advantage of nanoparticles of ellipsoidal shape with respect to spherical quantum dots arises from the additional geometrical characteristics related to shape-anisotropy parameter β ($\beta = c/a$ in which c and a are prolate ellipsoidal semi-axes). That effect makes possible the tuning of the spectral properties of objects of nanometre size. The tuneable control of spectral and optical characteristics of the nanometre objects through size and shape opens exciting possibilities for the engineering of new functional materials with a wide prospective application. Ellipsoidal nanoparticles thus play an important role for applications; the most promising candidates for further technological advances are precisely the ellipsoidally elongated objects of nanometre size. A comprehensive knowledge of the spectral and optical properties of ellipsoidally shaped nanoparticles is hence desirable.

In our recent papers [19,20], we considered a charged particle (electron or hole) confined within a potential well of ellipsoidal shape; the problem was solved in an effective-mass approximation. We assumed that a spherical potential well with infinitely high walls was subject to a deformation, which makes its shape that of a prolate ellipsoid. For a small deviation from the sphere the problem is solvable according to perturbation theory, with the unperturbed wave functions and energy levels corresponding to a spherical well. For an arbitrary deviation from a spherical shape the problem was solved using a direct diagonalization of the appropriate Hamiltonian. The energy levels and the corresponding wave functions have

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been thus obtained for the shape-anisotropy parameter β over a wide range. Using the obtained wave functions and energy levels, we calculated the optical-transition matrix elements in the dipole approximation. The transition-matrix elements involving the ground and first excited states are monotonic functions of β, whereas matrix elements involving the corresponding excited states have zeros and extrema that are reflected in the behaviour of their transition probabilities. Furthermore, some matrix elements involving the highly excited states have a discontinuity. This outcome is unexpected and requires comprehensive study to establish its origin and influence on the optical properties of nanoparticles. Although the existence of an effect of quantum confinement on the optical response of nanoparticles is well established, the fine structure of their emission and absorption spectra is incompletely studied.

For a diatomic molecule, only terms of distinct symmetry can intersect; the intersection of terms of like symmetry is impossible [21]. If, as a result of some approximate calculation, we obtain two intersecting terms of the same symmetry, they are found to move apart on calculating the next level of approximation. This result not only is true for a diatomic molecule but also is a general theorem of quantum mechanics; it holds for any case in which the Hamiltonian contains some parameter of which its eigenvalues are consequently functions [22].

In this work, we seek to show that the above-mentioned property of diatomic quasi-molecules is also characteristic for ellipsoidally shaped nanoparticles with a variable parameter. Explicitly, we show that for an ellipsoidally shaped nanoparticle some curves representing the highly excited energy levels of the same symmetry intersect for the some shape-anisotropy parameter β if the energy levels are calculated with perturbation theory; the intersection of these curves is impossible if the energy levels are obtained by a direct diagonalization of the appropriate Hamiltonian, i.e., when the interaction between the states is fully taken into account. We demonstrate that the intersection of the excited energy levels of the same symmetry leads to the discontinuity of the dipole-moment matrix elements involving the excited and ground states. Moreover, we explore the optical properties and show that the appearance of some features in the profiles of spectral lines emitted or absorbed by an ensemble of ellipsoidally shaped nanoparticles is caused entirely by the existence of minima and zeros in the appropriate dipole-moment matrix elements.

The article is organized as follows. After stating the purpose, we present briefly the basic equations in Sect. 2. The results of calculations are presented and discussed in Sects. 3 and 4, before a conclusion in Sect. 5.

2. Intersecting and non-intersecting energy levels

We consider a charged particle of effective mass m^* confined within a potential well of ellipsoidal shape with semi-axes $a = b$ and c:

$$\frac{x^2+y^2}{a^2}+\frac{z^2}{c^2}=1. \tag{1}$$

In (1) a represents the size of a well in directions x and y, c is the size in the direction z. The simplest potential $V(x, y, z)$ of that type is zero inside the ellipsoid and infinite on the surface of the ellipsoid and beyond. The corresponding Schrödinger equation that describes the motion of a particle trapped inside the ellipsoid, with the boundary condition for the wave function to be zero on the surface and outside the surface of the ellipsoid, reads:

$$\left[\Delta_{xyz}+K^2-\frac{2m^*}{\hbar^2}V(x,y,z)\right]\Psi(x,y,z)=0, \tag{2}$$

in which $K^2 = 2m^*E/\hbar^2$.

In new variables $\xi = xr_0/a$, $\eta = yr_0/a$ and $\varsigma = zr_0/c$, the boundary condition transforms from the surface of the ellipsoid to the surface of a sphere of radius $r_0 = (\xi^2+\eta^2+\varsigma^2)^{1/2}$. After writing the Laplace operator Δ_{xyz} in the new variables, we rewrite Eq. (2) as:

$$\left[\Delta_{\xi\eta\varsigma}+K^2-\alpha U(\xi,\eta,\varsigma)\right]\Psi(\xi,\eta,\varsigma)=0, \tag{3}$$

in which

$$U=\begin{cases}\dfrac{c^2(a^2-r_0^2)}{r_0^2(c^2-a^2)}\Delta_{\xi\eta\varsigma}+\dfrac{\partial^2}{\partial\varsigma^2} & \text{if } \xi^2+\eta^2+\varsigma^2<r_0^2,\\ \infty & \text{if } \xi^2+\eta^2+\varsigma^2\geq r_0^2,\end{cases} \tag{4}$$

and $\alpha = r_0^2(c^2-a^2)/(ac)^2$ is the parameter that reflects the deviation of the potential well from a spherical well. Parameter α is related to β according to $\alpha = r_0^2(1-\beta^{-2})/a^2$.

Transforming from coordinates ξ, η and ς to spherical coordinates $\xi = r\sin\vartheta\cos\varphi$, $\eta = r\sin\vartheta\sin\varphi$ and $\varsigma = r\cos\vartheta$ in Eqs. (3) and (4), we obtain an equation that describes the motion of a particle in the sphere:

$$\left[\Delta_{r\vartheta\varphi}+K^2-\alpha U(r,\vartheta,\varphi)\right]\Psi(r,\vartheta,\varphi)=0. \tag{5}$$

The problem of the motion of a charged particle in an ellipsoidal well thus reduces to the solutions of Eq. (5), in which effective potential $U(r, \vartheta, \varphi)$ is defined with Eq. (4) with $\Delta_{\xi\eta\varsigma}$ replaced with the Laplace operator written in spherical coordinates, and $\partial/\partial\varsigma = \partial/\partial r\cos\vartheta - r^{-1}\sin\vartheta\partial/\partial\vartheta$.

2.1. A perturbation approach

In a spherical potential well ($\alpha = 0$), the states of a particle are specified with quantum numbers n, l and m. Here l is the orbital quantum number and $m = 0, \pm1, \pm2, \ldots$ is the magnetic quantum number of the particle; n, which has no dependence on m, numbers the level in the spherical well for given l. The solutions of equation $(\Delta_{r\vartheta\varphi}+k_{nl}^2)\psi_{nlm}=0$ are well known and given in textbooks. The eigenfunctions are $\psi_{nlm}(r,\vartheta,\varphi) = C_{nl}j_l(k_{nl}r)Y_{lm}(\vartheta,\varphi)$, in which C_{nl} are normalizing factors, $j_l(k_{nl}r)$ are spherical Bessel functions and $Y_{lm}(\vartheta,\varphi)$ are spherical harmonics. The corresponding eigenvalues depend on the size of the potential well, r_0, and two quantum numbers n and l: $k_{nl}^2 = \tau_{nl}^2/r_0^2$, in which τ_{nl} is the nth root of a spherical Bessel function determined from the condition $j_l(k_{nl}r_0)\equiv j_l(\tau_{nl}) = 0$.

In Ref. [19] we assumed that αU is a small perturbation and solved Eq. (5) using perturbation theory. For the first-, second- and third-order corrections to the unperturbed energy, $E_{nl}^{(0)} = \hbar^2\tau_{nl}^2/(2m^*r_0^2)$, we obtained:

$$E_{nlm}=\left(\frac{r_0^2}{a^2}+\alpha E_{nlm}^{(1)}+\alpha^2E_{nlm}^{(2)}+\alpha^3E_{nlm}^{(3)}\right)E_{nl}^{(0)},$$

$$E_{nlm}^{(1)}=\frac{1-2l(l+1)+2m^2}{(2l-1)(2l+3)},$$

$$E_{nlm}^{(2)}=A_{l+2}^2B_{nl+2}^{(3)}+A_{l-2}^2B_{nl-2}^{(3)}, \tag{6}$$

$$E_{nlm}^{(3)}=\left(\frac{c^2(a^2-r_0^2)}{r_0^2(c^2-a^2)}-A_l\right)\left[A_{l+2}^2B_{nl+2}^{(4)}+A_{l-2}^2B_{nl-2}^{(4)}\right]\tau_{nl}^2.$$

In Eq. (6) A_l and $A_{l\pm2}$ are defined with expressions (A7) presented in Appendix A of Ref. [19]; $B_{nl\pm2}^{(s)} = \sum_{n'}\tau_{n'l\pm2}^2/(\tau_{nl}^2-\tau_{n'l\pm2}^2)^s$ is the infinite sum; τ_{nl} and $\tau_{n'l\pm2}$ are the roots of spherical Bessel functions $j_l(k_{nl}r)$ and $j_{l\pm2}(k_{n'l\pm2}r)$, respectively. For some states the energy levels calculated using Eq. (6) are given in Appendix A.

We introduce dimensionless quantity ε_{nlm} that is related to energy E_{nlm} through equation. Figure 1 shows ε_{131}, ε_{211} and ε_{151} as