

Confinement resonances in photoelectron angular distributions from endohedral atoms

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Both dipole and nondipole angular distribution parameters for photoelectrons emitted from the endohedral Ne@C₆₀ atom are investigated within both the framework of the Dirac bubble potential model and spherical, short range potential well of finite thickness ΔT . It is demonstrated, for 1s, 2s, and 2p photoelectrons of Ne, that because the fullerene shell acts as a resonator in this process, the energy dependence of the photoelectron angular distribution parameters differ considerably from that of the free Ne atom. For confined Ne, in contrast to the isolated Ne atom, these parameters as a function of photon energy acquire a significant resonance structure, owing to oscillations in the photoionization matrix elements induced by the fullerene shell.

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I. INTRODUCTION

The aim of this paper is to study how the C₆₀ fullerene shell influences the dipole and nondipole parameters of the photoelectron angular distribution resulting from photoionization of atoms encapsulated inside C₆₀, i.e., endohedral atoms, A@C₆₀.

Calculations performed in a number of papers [1–11] demonstrate that the fullerene shell acts as a resonator, causing the appearance of resonances termed *confinement* resonances [12] in the energy dependence of the total photoionization cross sections of the atom, which without the C₆₀ shell would be structureless and smooth. It has also been found [13] that the encapsulation of a hydrogen atom (or hydrogenic ion) leads to the appearance of resonance structure in nondipole photoelectron angular distribution parameters. However, the effect of the C₆₀ cage on photoelectron angular distribution asymmetry parameters of an endohedral nonhydrogenic atom, A@C₆₀, has not yet been studied. To remedy this situation, we investigate photoelectron angular distribution asymmetry parameters upon photoionization of the 1s, 2s, and 2p subshells of Ne in endohedral Ne@C₆₀.

The description of the interaction of electromagnetic radiation with fullerene-like molecules is a much more complicated theoretical problem than that for an isolated atom. Therefore, to get some idea of the influence of the fullerene shell surrounding an encapsulated atom, considerable simplifications are useful. One of simplifications comes from the fact that the radius of the fullerene cage is significantly bigger than the radius of any subshell of the encapsulated atom. Thus, to a good approximation, wave functions of the bound atomic electrons in an endohedral A atom are the same as those in the isolated atom A. As for the carbon atoms from the C₆₀ cage, their role is only to modify the final state of the photoionization process, the molecular continuum wave function.

Furthermore, when the wavelength of the slow photoelectron significantly exceeds the distances between the carbon

atoms of the C₆₀ cage, the actual potential of the C₆₀ can be replaced by an effective potential acting on the electron like a continuous medium. For this medium one can introduce the concept of the coefficient of reflection or refraction of an electronic wave (see, e.g., Ref. [14]). Therefore, it is expected that the slow photoelectron will perceive the fullerene cage C₆₀ as an unstructured semitransparent spherical shell that generates a reflected electronic wave inside the sphere and a transmitted wave outside. This was conclusively demonstrated earlier [15] where the photoelectron angular distribution was calculated for A@C₆₀ photoionization near threshold. The fullerene cage was realistically represented as a set of nonoverlapping atomic potentials due to each of the 60 carbon atoms; it was found that, for low energy photoelectrons, the shape of the photoelectron angular distribution coincides with the differential photoionization cross section of an isolated atom. This is possible only when the photoelectron moves in a spherically symmetric potential. Consequently, for low energy photoelectrons, the fullerene cage C₆₀ is perceived by the photoelectron as a structureless, spherical potential well $V(r)$. In the present paper, we deal only with the case of low energy photoelectrons, i.e., we restrict ourselves to the consideration of near-threshold photoionization. Thus, replacing the actual potential of the fullerene cage by a central potential is a reasonable approximation.

Experimental studies of endohedral atoms A@C₆₀ show that noble gas atoms [16] and group-V atoms [17], are, as a rule, located at the center of the fullerene cage without any charge transfer to the cage. It is the very small van der Waals forces that cause the atom to be located at the center of the cage. These van der Waals forces are quite weak, compared to atomic (Coulomb) forces, so they do not alter the ground state wave function of the atom A appreciably. Since we consider the endohedral fullerene Ne@C₆₀ in this paper, based on the above results, we can reliably take the position of the Ne atom to be at the center of the cage.

An important feature of the C_{60} potential well is the presence of a shallow level—shallow compared with the effective depth of this well. According to the experimental data [18], the electron affinity I of the C_{60} is $I \sim 2.65$ eV while the effective depth of the well $V_0 \approx 8.2\text{--}11.5$ eV [8,11]. This allows us to describe the wave function of the slow photoelectron inside and outside the fullerene shell by correctly chosen boundary conditions that depend only on experimental parameters; the fullerene's radius R and electron affinity I . The situation here is similar to nuclear physics, where low energy nucleon scattering can be described by a logarithmic derivative of the wave function [19]. It is well known that a suitable mathematical method to impose the necessary boundary conditions is to introduce into the Schrödinger equation the so-called Dirac bubble-potential $V(r) = -V_0\delta(r-R)$ instead of the actual C_{60} potential. This potential has been used previously to describe photodetachment of negative C_{60}^- ions [20], elastic scattering of slow electrons by fullerenes [21], and confinement resonances in the dipole angle-integrated photoionization cross sections of endohedral atoms $A @ C_{60}$ [9,10].

In this paper, we use the Dirac bubble potential to study the dependence of the dipole $\beta(\omega)$ and nondipole $\gamma(\omega)$ parameters [22] of the photoelectron angular distribution from endohedral atoms on photon energy, ω . We demonstrate that these parameters, as functions of the photon energy, acquire significant resonance structures, making them large, owing to the appearance of *confinement* resonances in the photoionization matrix elements induced by the spherical shell potential of C_{60} .

For photoelectrons of energy higher than that of near-threshold photoelectrons, the noncentral nature of the molecular potential [5,6,15] due to the C_{60} shell becomes important. As a consequence, this may lead to the appearance of additional resonances—*molecular* resonances arising in the photoionization spectra of endohedral atoms [5,6]. Both types of resonances, confinement and molecular resonances, should coexist in the spectra independently, unless they accidentally overlap which is unlikely because each should be important in a different energy region.

II. THEORY AND DISCUSSION

The formulas employed in this paper were derived earlier [9,10]. Therefore, herein, we give only the main results. For an atom A located at the center of a C_{60} cage, the problem of calculating the photoelectron wave function in the continuum reduces, in a one-electron approximation, to solution of a one-dimensional Schrödinger equation where the Dirac bubble potential is added to the potential of an isolated atom A . Evidently, solutions of this equation inside and outside a sphere of radius R correspond to wave functions calculated in the field of an isolated atom A . Therefore, inside the confining potential the continuum wave function $\chi_{kl}(r)$ differs from the regular solution $u_{kl}(r)$ of the Schrödinger equation for a free atom only by a normalization factor $D_l(k)$, where k is the photoelectron momentum and l is the orbital quantum number. Correspondingly, $\chi_{kl}(r) = D_l(k)u_{kl}(r)$. Outside the δ potential, the function $\chi_{kl}(r)$ is a linear combination of the

regular $u_{kl}(r)$ and irregular $v_{kl}(r)$ solutions of this equation. The coefficients of the linear combination are defined by matching conditions for the wave functions imposed on the surface of the spherical shell, i.e., at $r=R$. Then, both a wave function phase shift $\delta_l(k)$, due to the electron scattering on the δ -function potential, and the factor $D_l(k)$ are given by

$$\tan \delta_l(k) = \frac{u_{kl}'^2(R)}{u_{kl}(R)v_{kl}(R) - k/\Delta L}, \quad (1)$$

$$D_l(k) = \left[1 - \frac{v_{kl}(R)}{u_{kl}(R)} \tan \delta_l(k) \right] \cos \delta_l(k), \quad (2)$$

where, ΔL is the jump of the logarithmic derivative of the wave function at $r=R$ given by $\Delta L = -2V_0 = -\beta(1 + \coth \beta R)$, where $\beta = \sqrt{2I}$ with I being the electron affinity of C_{60} . [Here and throughout the text the atomic system of units ($\hbar = m = e = 1$) is used.] Note, in derivation of Eq. (2) we took into account that the Wronskian of the radial Schrödinger equation is $W_{kl} = u_{kl}(r)v_{kl}'(r) - u_{kl}'(r)v_{kl}(r) = k \neq 0$.

As long as the “size,” of the atomic subshell is smaller than the size of the C_{60} , the matrix elements for electron transitions to the continuum are formed near atom A , i.e., well inside the C_{60} cage. Therefore, these amplitudes coincide with the amplitudes of the corresponding transitions in the free atom except for the multiplicative factor $D_l(k)$. Because of the coupling between the oscillations of the wave functions inside and outside the cage, the coefficients $D_l(k)$ have a resonance character. Therefore, there are resonances, the confinement resonances, in the transition matrix elements for endohedral atoms that translate into resonances in the total photoionization cross section [9,10].

It is evident that for the same reason the confinement resonances will appear also in the dipole and nondipole asymmetry parameters. As noted, this was seen for endohedral hydrogenic atoms and ions [13]. The expressions for these parameters can be simply obtained [9,10] from the general expressions for the dipole and nondipole asymmetry parameters derived for free atoms where it is only necessary to replace the dipole $R_{l\pm 1}$ and quadrupole $Q_{l\pm 2,0}$ matrix elements by $R_{l\pm 1} \rightarrow D_{l\pm 1}R_{l\pm 1}$ and $Q_{l\pm 2,0} \rightarrow D_{l\pm 2,0}Q_{l\pm 2,0}$, respectively, and the corresponding phase shifts of the photoelectron wave functions for the free atom $\Delta_{l\pm 1}(k)$ and $\Delta_{l\pm 2,0}(k)$ by the sum of the phases: $\Delta_{l\pm 1} \rightarrow \tilde{\Delta}_{l\pm 1}(k) = \Delta_{l\pm 1}(k) + \delta_{l\pm 1}(k)$ and $\Delta_{l\pm 2,0}(k) \rightarrow \tilde{\Delta}_{l\pm 2,0}(k) = \Delta_{l\pm 2,0}(k) + \delta_{l\pm 2,0}(k)$.

We focus both on the dipole parameter $\beta_p(\omega)$ defining the angular distribution in photoionization of the p atomic subshells [for s subshells $\beta(\omega) = 2$] and nondipole parameter $\gamma_s(\omega)$ defining the differential cross section of photoionization of the s subshells. For these cases [23]:

$$\beta_p(\omega) = 2D_2R_2 \frac{[D_2R_2 - 2D_0R_0 \cos(\tilde{\Delta}_2 - \tilde{\Delta}_0)]}{(D_0^2R_0^2 + 2D_2^2R_2^2)}, \quad (3)$$

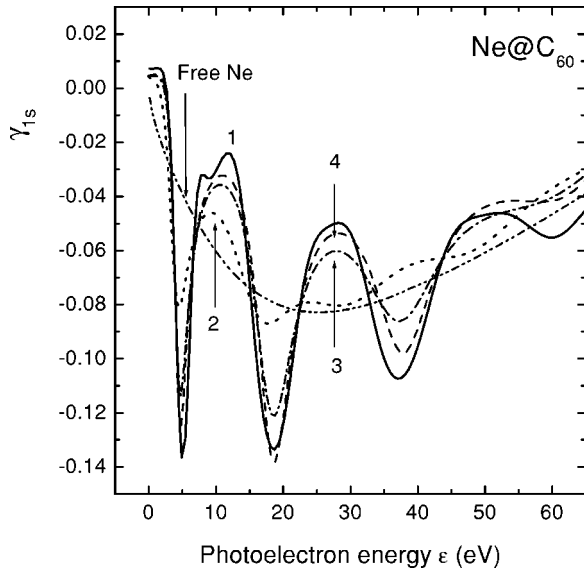


FIG. 1. Nondipole asymmetry parameter $\gamma_{1s}(\epsilon)$ as a function of the photoelectron energy $\epsilon = k^2/2$ for $1s$ photoionization of $\text{Ne}@C_{60}$ calculated within two different approximations. (1) the δ -potential model (the present theory). (2),(3),(4) the model of a spherical, short range potential well of inner radius R_{in} , finite thickness ΔT , and depth U_0 (Ref. [8]), as follows: (2) $R_{in}=5.75$ a.u., $U_0=-0.3027$ a.u., $\Delta T=1.89$ a.u.; (3) $R_{in}=6.139$ a.u., $U_0=-0.5099$ a.u., $\Delta T=1.0$; (4) $R_{in}=6.389$ a.u., $U_0=-0.9515$ a.u., $\Delta T=0.5$ a.u.

$$\gamma_s(\omega) = 6 \frac{\omega D_2 Q_2}{c D_1 R_1} \cos(\tilde{\Delta}_2 - \tilde{\Delta}_1), \quad (4)$$

where c is the speed of light. Since the photoelectron angular distribution parameters involve interference among amplitudes of different angular momenta, rather than just the sum of absolute squares that determines the total photoionization cross section, one can expect in the energy dependence of these parameters and, hence, in the photoelectron angular distributions, more complicated resonance structures than in the total photoionization cross sections.

Equations (1)–(4) were applied to the photoionization of the $\text{Ne}@C_{60}$ endohedral atom. The wave functions of the free Ne atom in $1s$, $2s$, $2p$ states, and the continuum $u_{kl}(r)$, were calculated in the one-electron Hartree–Fock approximation using the computing codes ATOM [24]. The irregular at $r=0$ solutions $v_{kl}(r)$ were calculated, as in Refs. [9,10], using

$$v_{kl}(r) = u_{kl}(r) W_{kl} \int \frac{dr}{u_{kl}^2(r)}. \quad (5)$$

The calculated results of the dipole and nondipole parameters for the photoionization of the Ne atom encapsulated in a C_{60} shell are presented in Figs. 1–3. The corresponding parameters for the free Ne atom are also given.

Clearly, the fullerene shell qualitatively alters the dependence of these parameters on the photoelectron energy. For the free Ne atom, these parameters are smoothly changing with energy. However, for the endohedral Ne atom, the dependence is dramatically different showing the appearance of

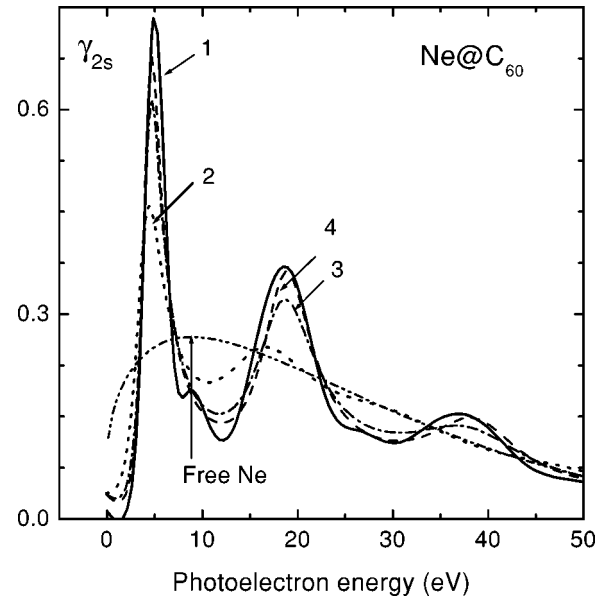


FIG. 2. Nondipole asymmetry parameter $\gamma_{2s}(\epsilon)$ for $2s$ photoionization of $\text{Ne}@C_{60}$ calculated within the δ -potential theory (line 1) and the SW model (lines 2, 3, and 4) with the same choice of R_{in} , ΔT , and U_0 as in Fig. 1.

a significant resonance in these parameters. Amplitudes of the resonances rapidly decrease with the growth of the photoelectron energy and almost vanish at about 50 eV.

Also, for comparison with the δ -potential model, in all the presented figures shown are calculated results obtained by modeling the C_{60} cage by the spherical, short range potential well (SW) of inner radius R_{in} , finite thickness ΔT , and depth U_0 [8]. These are calculations performed with three deca-

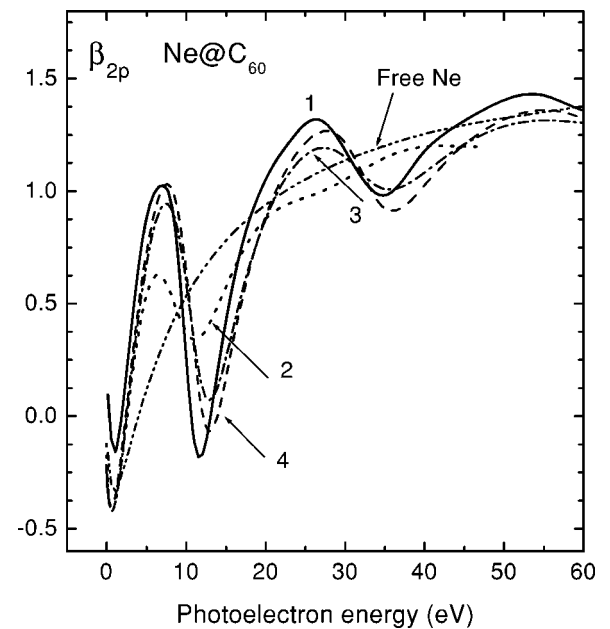


FIG. 3. Dipole asymmetry parameter $\beta_{2p}(\epsilon)$ for $2p$ photoionization of $\text{Ne}@C_{60}$ calculated within the δ -potential theory (line 1) and the SW model (lines 2, 3, and 4) with the same choice of R_{in} , ΔT , and U_0 as in Figs. 1 and 2.

ing values of ΔT ($\Delta T=1.89, 1.0$, and 0.5 a.u.), to explore the convergence of photoelectron angular asymmetry parameters to those calculated within the δ -potential model for which, naturally, $\Delta T=0$. For each calculation with the changed ΔT , the depth U_0 of the potential well and its inner radius R_{in} were changed appropriately as well, to keep the $1s$ electron affinity in a negatively singly charged C_{60} constant and equal to its experimental value $I=2.65$ eV. Adjusted values of U_0 and ΔT are in figure captions. These figures convincingly demonstrate that, with decreasing ΔT , results of calculations performed within the SW model rapidly converge to results obtained within the δ potential, by this showing the equivalency between the two models at low photoelectron energies. Both models show that the fullerene shell acts as a resonator generating oscillations in the energy dependence of photoelectron angular distribution parameters. Note, the calculations are extended to photoelectron energies far exceeding the low-energy range of applicability of the δ -potential model, simply to illustrate that confinement resonances in the parameters are fading away rapidly with increasing energy of photoelectrons.

Physically, the origin of the observed confinement resonances is as follows. The photoelectron can escape from the atom directly, or be scattered by the C_{60} shell on its way out. When the waves representing these two “pathways” are in phase, constructive interference, a resonant enhancement, results. When they are out of phase, destructive interference occurs. Since the relative phases of the two waves are energy dependent, the interference is also energy dependent, which is clearly seen in the calculated results. Generally, the physical origin of these confinement resonances is the same as the cause of EXAFS in the photoabsorption of condensed matter, and the similar phenomenon in diatomic (and other) molecules. The decrease in the resonance structure with increasing photoelectron energy occurs because the C_{60} cage becomes more and more transparent to the photoelectron, thereby decreasing reflection and, thus, interference.

Note that the phenomenon of resonance behavior of the asymmetry parameters in the photoelectron angular distribution considered herein gives a qualitative explanation of the observation of anomalously high values of the nondipole asymmetry parameters in diatomic molecules [25]. Indeed, consider photoionization of an inner subshell of the atom A in a diatomic molecule AB in the gas phase, i.e., with random orientation of the molecular axis relative to the polarization

vector of the radiation. The atom B remains neutral in this process and is arbitrarily located on the sphere with the center at the nucleus of the atom A with radius equal to the interatomic distance in this molecule. In lowest order, the effect of the atom B on the photoionization parameters can be approximated by the introduction of a spherically symmetric potential that represents the atom B smeared over the surface of this sphere. Then, the situation for this molecule becomes, to a large extent, similar to the situation discussed above for an endohedral atom. For an isolated atom A the ratio between the quadrupole and dipole matrix element has a value of the order of the radius of the ionized atomic subshell, while for the same atom in the molecule this ratio, as seen from Eq. (4), is multiplied by the ratio D_2/D_1 for the quadrupole and dipole parts of the photoelectron wave function. The values of D_1 and D_2 , which are defined by the conditions of reflection and refraction of the photoelectron wave function on the potential sphere, are such that this ratio can be significantly more than one, as demonstrated in Fig. 2. This resonant enhancement is the likely qualitative explanation for the significant increase in the nondipole asymmetry parameter recently observed in the N_2 molecule [25]. We emphasize that these considerations apply to an ensemble of randomly oriented molecules, thereby being equally valid for both hot (high- J rotational states) and cold (low- J rotational states) gases.

In addition, note that the oscillations of the dipole and nondipole angular anisotropy parameters, presented herein for Ne in $Ne@C_{60}$, should be general and qualitatively similar for any endohedral atom. We strongly urge the initiation of experimental investigations of these asymmetry parameters to establish the existence of this kind of resonance, the confinement resonance, which could have important implications for the interpretation of molecular and condensed matter photoelectron studies.

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