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Comment on "Photoionization of endohedral atoms using *R*-matrix methods: Application to Xe@C$_{60}$"

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We demonstrate that what is called a total photoionization cross section in the work by T. W. Gorczyca, M. F. Hasoglu, and S. T. Manson [Phys. Rev. A **86**, 033204 (2012)] is in fact a partial photoionization cross section. These quantities differ impressively even in isolated atoms. This demonstrates the prominent role of inelastic collisions of a photoelectron from an intermediate or inner shell not mentioned in their paper. We discuss briefly the correspondence between the experimental data, theoretical predictions, and *R*-matrix results from Phys. Rev. A **86**, 033204 (2012). We call attention to the danger in using parameters of C$_{60}$ potential selected by fitting the same experimental data that one wants to describe. We show that our criticism is applicable to the theoretical part of the most recent publication on photoionization of Xe@C$_{60}^{+}$ [R. A. Phaneuf *et al.*, Phys. Rev. A **88**, 053402 (2013)].

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Recently, we ran across a paper [1] that is dedicated to describing the *R*-matrix approach to endohedral photoionization, using as a concrete object of application the endohedral Xe@C$_{60}$. The authors of [1] started by considering the total photoionization of a Xe atom above its $4d^{10}$-subshell photoionization threshold (Fig. 2 in [1]). They show in the figure that a big discrepancy exists between the experimental data from [2] (their [44]) and the random-phase approximation with exchange (RPAE) calculations from [3] (their [45]). In fact, Fig. 1 of [1] compares the RPAE results for total cross section with the partial photoionization contribution from channels $4d-\varepsilon f,p$, measured in [2]. These results, as was demonstrated in [3], should be different. The difference, which is about 30%, is attributed in [3] to the so-called intra-atomic friction due to inelastic photoelectron scattering. The account of this effect by inclusion of emission of only one extra electron, led to (demonstrated in Fig. 1) complete agreement between the independently obtained results of calculations [3] (solid line) and the experimental data [2] (dots). Note that already for the isolated atom *R* matrix gives a difference between results in so-called "length" and "velocity" forms of about 30%, which signals internal inaccuracy. This inaccuracy is much bigger than what was already achieved long ago in describing photoionization of noble gases. This difference signals either numerical inaccuracy or neglect of essential physical effects. Perhaps it reflects the choice, to some extent arbitrary, of the so-called "box radius" a in the *R*-matrix approach.

As to the total cross sections, very good agreement with experiment has long been known to exist in RPAE, including an almost total coincidence of "length" and "velocity" results [4]. Our Fig. 1 is similar to Fig. 2 from [1], differing from it by an additional, solid curve from [3] (in red) that is, however, very important. This curve, when compared to the experimental data shows that the partial photoionization cross section of the Xe atom above its $4d^{10}$-subshell threshold was well explained in [3].

Note that in [3] the reasons were clarified as to why RPAE is close to the total photoabsorption cross section and differs from contributions of only the $4d-\varepsilon f,p$ channels. Namely, this is because RPAE cross sections automatically include two-step processes such as primary $4d$ photoionization as a first step with subsequent "on the energy shell" inelastic scattering of the photoelectrons $\varepsilon f,p$ upon the residual ion with $5p$ and $5s$ subshell ionization as the second step.

Now let us discuss the photoionization of Xe@C$_{60}$. The first prediction of Xe $4d$ giant resonance destruction under the action of the fullerenes shell that preserved the Xe giant resonance sum rule has been made in the frame of RPAE, i.e., for the total photoionization cross section in papers [5,6] and confirmed at least qualitatively in [7]. The preservation of the sum rule of a given deep enough subshell is very important since interaction with the loosely bound electrons in C$_{60}$ cannot affect this integral characteristic considerably.

According to the point of view of the authors of [7], there the total photoionization cross section of Xe@C$_{60}^{+}$ was presented. Since only one channel was in fact measured, to compare the data obtained with the theoretical calculations, the latter were divided by a factor of 10. The results were presented as Fig. 4 in [7]. It is seen there that the agreement between calculations [5,6] divided by 10 and measurements in [7] are qualitatively reasonable. The photoionization cross section for Xe@C$_{60}^{+}$ in [7] oscillates around the total photoabsorption cross section divided by 10, preserving the $4d^{10}$ sun rule. Our Fig. 2, although differently scaled, illustrates the situation.

The experiment, according to what is written in [7], was specially designed to check the validity of the predictions made in [5]. The data extracted from [7] are presented in Fig. 3 of [1], being, however, stripped of all previous calculation data, including that of [5,6]. In Fig. 3 of [1] the normalization factor is, however, 6.5 and not 10 as in [7], and the comparison is made with the partial of the $5p^{-1}ks$, $5p^{-1}kd$, $5s^{-1}kp$, $4d^{-1}kp$, and $4d^{-1}kf$ channels, but not the total photoionization cross section.

The parameters of the square well C$_{60}$ potential in [1] differ essentially from those that are generally accepted. Instead, they were specially chosen to reproduce as well as possible [8]

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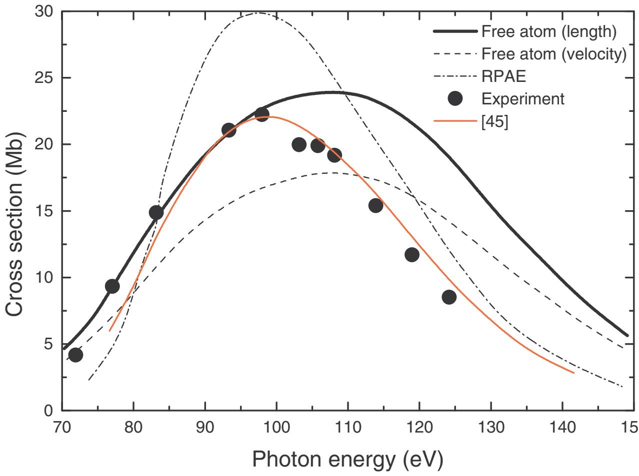

FIG. 1. (Color online) Photoionization cross section of the Xe atom above the $4d$-subshell ionization threshold. RPAE: total photoabsorption cross-section [4] (not [3], or [45], as is cited in [1]); solid and dashed lines: R-matrix calculations in "length" and "velocity" forms from [1]; red line: calculation for partial $4d-\varepsilon f,p$ photoionization cross section [3]; dots: experiment for partial $4d-\varepsilon f,p$ photoionization cross section [2] ([44] in [1]). This is not the total photoionization cross section of the Xe atom, as stated in [1].

the experimental data [7]. This is not a reliable approach when one deals with new, not widely confirmed experimental data.

The experiment was performed on $Xe@C_{60}^{+}$ instead of $Xe@C_{60}$. This makes, of course, the theory-experiment comparison less direct. However, the same problem is valid for [1] and for [5,6], with the essential difference being that [5,6] was a prediction, while [1] followed the existing data.

Incidently, in the frame of time-dependent density-functional approach that was the first prediction for the $Xe@C_{60}$ photoionization cross section [9], the giant resonance sum rule is violated by a factor obviously more than 2 (less than 5 instead of 10; see Fig. 4 of [9]), the oscillations are weak, and the cross-section maximum is only 12 Mb.

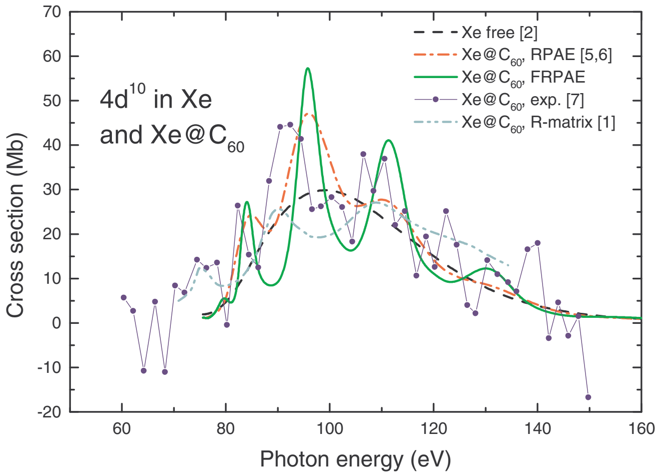

FIG. 2. (Color online) Photoionization cross section of $Xe@C_{60}$ and free Xe in the region of Xe $4d^{10}$ giant resonance. The red curve is from [5,6] that is omitted in Fig. 3 of [1].

One can say that [1] is dedicated not to describing photoionization of a rather complex concrete object $Xe@C_{60}^{+}$ but to developing the R-matrix approach per se, so it can limit itself by presenting only the R-matrix approach with the ability to deal somehow with the existing experimental data. From our point of view, such logic is, however, questionable.

The experiment is still far from being quantitatively perfect. It demonstrates that qualitatively the predictions in [5,6] were correct, but still a lot has to be done from both the theoretical and experimental sides to achieve an understanding of the complicated dynamics of the atom-fullerenes shell interaction in order to achieve reasonable quantitative agreement between theory and experiment. As of now, the R-matrix results in [1] are no better than those in [5,6], in spite of adding adjustable parameters, and specifically for this approach suffer from a hidden parameter—the choice of the "box radius," where inner and outer wave functions are sewed.

On the other hand, R matrix is in principle a precise approach that has the possibility of improving the already achieved description, while RPAE is by definition an approximation. However, the materialization of the R-matrix ability of precise description of such systems as isolated multielectron atoms, not to mention much more complex endohedrals, goes well beyond a simple variation of the effective one-electron static potential parameters.

Recently, we became aware of the paper [10], where new essential experimental results on photon absorption by $Xe@C_{60}^{+}$ were presented. It was demonstrated that the total photoabsorption cross section is a sum of several almost equal contributions of inelastic processes, in which ionization of $4d$ Xe is accompanied by elimination of one or several carbon atoms from the fullerenes shell. The measured cross section confirms the pioneered results of [7], but gives smaller amplitude of oscillations due to the effect of the fullerenes shell than in [7].

The results of [10] qualitatively confirm the theoretical predictions in [5,6]. The observed total oscillator strength now equals $f = 6.2 \pm 1.4$, which is considerably bigger than that detected in the first observations [7]. We do believe that subsequent measurements will help to understand the nature of the yet missed part of the highly probable total oscillator strength 10 that is correct for the isolated Xe $4d^{10}$ subsell.

Paper [10] also has a theoretical part that is written, as far as we understand, by the same authors as [1]. They presented a new, relativistic version of the R-matrix approach that was applied to the $4d$ subshell both in Xe and $Xe@C_{60}^{+}$. In Fig. 1 of [10] they demonstrate excellent agreement between the results of the relativistic R-matrix calculations for the cross section of the reaction $\gamma + \mathrm{Xe} \rightarrow e + \mathrm{Xe}^{+}$, i.e., one-electron photoionization, and the experimental total photoabsorption cross section (see, e.g., [2]). As we have already discussed above in this Comment and also much earlier [3], both experiment [2] and calculation [3] results are essentially different for total and one-electron cross sections, respectively.

By choosing parameters of the effective fullerenes potential (relativistic effects are small enough in $4d$ Xe), very good agreement is achieved between renormalized to

$f = 10$ experimental data and R-matrix calculations for $\gamma + \mathrm{Xe}@\mathrm{C}_{60}^{+} \rightarrow e + \mathrm{Xe}^{+}@\mathrm{C}_{60}^{+}$. In view of this Comment and the results obtained in [2,3], the meaning of achieving almost ideal coincidence between one-electron calculated and total experimental cross sections of $\mathrm{Xe}@\mathrm{C}_{60}^{+}$ photoionization is unclear to us.

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