Hybridization-related correction to the jellium model for fullerenes

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Abstract
We introduce a new type of correction for a more accurate description of fullerenes within the spherically symmetric jellium model. This correction represents a pseudopotential which originates from the comparison between an accurate \textit{ab initio} calculation and the jellium model calculations. It is shown that such a correction to the jellium model allows one to account, at least partly, for the \(sp^2\)-hybridization of carbon atomic orbitals. Therefore, it may be considered as a more physically meaningful correction as compared with a structureless square-well pseudopotential which has been widely used earlier.

(Some figures may appear in colour only in the online journal)

1. Introduction
Since the discovery of fullerenes by Kroto \textit{et al} [1] in 1985, these molecules have been the objects of intensive experimental and theoretical investigations (see, e.g., [2]). At present, the investigation of fullerenes is active since they are proposed to be used in various fields of science and technology. For instance, excitation of fullerenes, placed in a biological medium, by an external radiation or incident heavy ions may lead to an active generation of secondary electrons or reactive oxygen species. This allows fullerenes to be potentially used as sensitizers in photodynamic therapy [3]. A very important fundamental problem closely related to the aforementioned application is an adequate description of dynamic response of fullerenes to external fields or to the interaction with projectiles. Processes of scattering of electrons, photons and heavy charged particles on various atomic clusters and fullerenes, in particular, have been actively studied during the past several decades (see, e.g., the review [4] and references therein). Not the least of the factors for a proper description of the dynamic response of a many-electron system is an adequate description of the ground- and excited-state (including excitation into continuum) properties of the system under study.

Contemporary software for quantum-chemical calculations (e.g., Gaussian 09 [5]) provides an accurate quantitative description of the ground state of many-particle systems (fullerenes, in particular), and allows one to obtain information on geometrical and chemical properties of the system. However, the description of dynamic properties, which play an important role in the process of photoionization, by means of such programs faces significant difficulties. Dynamic properties (e.g., dynamic polarizability) are closely related to the response of a many-electron system to an external electromagnetic field. In many cases, the properties are governed by a collective excitation of electrons and the formation of plasmon resonances in the excitation spectra [6]. In various systems plasmon resonances lie either below the ionization threshold (in metal clusters) or above it (e.g., in fullerenes). Out of these two classes of atomic clusters, only the optical response of metal clusters has been calculated so far with the help of quantum-chemical programs (see, e.g., [7, 8]). Collective electron excitations in fullerenes, which lie in the continuous spectrum, have not been described so far by means of quantum-chemical programs. However, this can be achieved within simplified model approximations. A minimum requirement is that these approximations must

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provide an accurate quantitative description of the ground-state features of the systems under study, in order to be applied to the investigation of the dynamic response and to the calculation of the photoabsorption (or, in particular, photoionization) spectrum.

One of the well known and widely used approaches is based on the jellium model [9]. It was applied frequently to the description of ground-state properties of metal clusters [9–11] and fullerenes [12, 13], as well as to the investigation of photoexcitation processes arising in these systems [13–21].

In [12, 22], it was stated that the ground-state properties of fullerenes cannot be described properly by the standard jellium model which produces, in particular, unreliable values for the total energy [12]. To avoid this, adding of structureless pseudopotential corrections was suggested [12]. As a rule, a phenomenological square-well (SW) pseudopotential has been commonly used in the calculations [12, 16, 18, 21]. It was claimed that accounting for such a pseudopotential increases the accuracy of the jellium-based description [16] and, for instance, allows one to reproduce the experimental shape of photoabsorption (or, in particular, photoionization) spectrum.

It was claimed that accounting for such a pseudopotential choice of parameters of the used SW pseudopotential have not been clearly justified so far from a physical viewpoint. Therefore, a detailed ionic structure of the systems under study is substituted by the uniform spherically symmetric a many-electron system is considered as a sum of two interacting subsystems: a valence electrons subsystem and a positively charged ionic core. One of the stable isomers of C20 corresponds geometrically to the regular dodecahedron [23] and, like the truncated icosahedron C60, has the symmetry of the Ih point group which is very close to spherical symmetry. Therefore, a detailed ionic structure of the systems under study is substituted by the uniform spherically symmetric distribution of the positive charge, in the field of which the motion of the valence electrons is considered [9].

The valence 2s^22p^6 electrons in each carbon atom form a cloud of delocalized electrons, while the inner-shell 1s^2 electrons are treated as frozen and not taken into consideration. Thereby, we consider 240 delocalized electrons in C60 and 80 electrons in C20. The valence electrons are moving in a spherically symmetric central field, so one can construct the electronic configuration described by the unique set of quantum numbers \( n, l \) where \( n \) and \( l \) are the principal and orbital quantum numbers, respectively.

Since it is commonly acknowledged [24–26] that C60, as well as other fullerenes, is formed from fragments of planar graphite sheets, it is natural to match the \( \sigma \)- and \( \pi \)-orbitals of graphite to the nodeless and the single-node wavefunctions of a fullerene, respectively [27]. Carbon atoms within a graphite sheet are connected by \( \sigma \)-bonds, whereas different sheets are connected by \( \pi \)-bonds. In the fullerene, the nodeless \( \sigma \)-orbitals are localized at the radius of the ionic core while the single-node \( \pi \)-orbitals are oriented perpendicularly to the fullerene surface. The ratio of \( \sigma \) - to \( \pi \)-orbitals in C60 should be equal to 3 : 1 due to the \( sp^2 \)-hybridization of carbon orbitals [28]. Thereby, the electronic configuration of the delocalized electrons in C60 is written in the form [13]:

\[
\begin{align*}
1s^22p^63d^{10}4f^{14}5g_{18}6h_{10} & = 2s^23p^64d^{10}5f^{14}6g_{18}7h_{10}.
\end{align*}
\]

Radial wavefunctions of the 1s \( \cdots \) 10m shells are nodeless, while the wavefunctions of the 2s \( \cdots \) 7h shells have one radial node each.

Using the same methodology, one defines the electronic configuration of the 80 delocalized electrons in C20 as follows:

\[
\begin{align*}
1s^22p^63d^{10}4f^{14}5g_{18}6h_{10}2s^23p^64d^{10}5f^{2}.
\end{align*}
\]

Within the jellium model the fullerene core of the charged carbon ions, C\(^{4+}\), is described as a positively charged spherical layer of a finite thickness \( \Delta R = R_2 - R_1 \). The thickness \( \Delta R \) is chosen to be equal to 1.5 Å which corresponds to a typical diameter of a carbon atom [29] and refers to experimental data from [18]. The potential of the core may be written as

\[
U_{\text{core}}(r) = -\frac{N}{r} + \frac{3}{2} R_2^2 \left( \frac{R_1}{R_2} - 1 \right) \left( \frac{1}{R_1^2 - r^2} \right) \left( 1 + \frac{2R_3}{r^2} \right) + \frac{r}{R_1} \left( 1 - \frac{3}{2} \right) \frac{R_1^2 - R_2^2}{R_1^2 - r^2},
\]

where \( N \) is the number of delocalized electrons in a fullerene \((N = 240 \text{ in } C_{60} \text{ and } N = 80 \text{ in } C_{20})\), \( R_1 = R - \Delta R/2 \) and \( R_2 = R + \Delta R/2 \) with \( R \) standing for a fullerene radius \( R_{\text{C60}} = 3.54 \text{ Å} \) and \( R_{\text{C20}} = 2.04 \text{ Å} \) [30].

The electronic subsystem is treated within the local density approximation (LDA). Single-electron wavefunctions \( \phi_{nlm}(r) \) and the corresponding energies \( \epsilon_{nlm} \) are determined from a system of self-consistent Kohn–Sham equations:

\[
-\frac{\Delta}{2} + U_{\text{eff}}(r) \phi_{nlm}(r) = \epsilon_{nlm} \phi_{nlm}(r),
\]

The atomic system of units, \( m = |e| = \hbar = 1 \), is used throughout the paper.

## 2. Methods of Investigation

### 2.1. Jellium Model

In this paper, the fullerenes C\(_{60}\) and C\(_{20}\) are treated within the jellium model which is based on an assumption that a many-electron system is considered as a sum of two interacting subsystems: a valence electrons subsystem and a positively charged ionic core. One of the stable isomers of C\(_{20}\) corresponds geometrically to the regular dodecahedron [23] and, like the truncated icosahedron C\(_{60}\), has the symmetry of the Ih point group which is very close to spherical symmetry. Therefore, a detailed ionic structure of the systems under study is substituted by the uniform spherically symmetric distribution of the positive charge, in the field of which the motion of the valence electrons is considered [9].
The total electrostatic potential of the system is represented as a sum of the nuclear and electronic parts:

\[ U_{\text{tot}}(r) = U_n(r) + U_d(r) = - \sum_{A} \frac{Z_{A}}{|r - \mathbf{R}_{A}|} + \int \frac{\rho(r')}{|r - r'|} \, dr'. \tag{8} \]

The electron density \( \rho(r) \) and the potential \( U_n(r) \) created by all carbon ions, \( C^{4+}(1s^2) \), were extracted from the Gaussian output file with the help of the Multiwfn software \[33\]. The potential \( U_d(r) \) created by the delocalized electrons was calculated separately using the extracted electron density.

The jellium model treats the fullerences \( C_{60} \) and \( C_{20} \) as spherically symmetric objects while a more precise \( \textit{ab initio} \) calculation accounts for the real icosahedral symmetry of the molecules. Therefore, to draw an analogy between the two

\[ U_{\text{eff}}(r) = U_{\text{core}}(r) + \int \frac{\rho(r')}{|r - r'|} \, dr' + U_{\text{XC}}^{\text{LDA}}(r), \tag{3} \]

\[ \rho(r) = \sum_{nl} \sum_{m=-l}^{l} \frac{N_{nl}}{2(2l + 1)} |\phi_{nlm}(r)|^2, \tag{4} \]

where \( N_{nl} \) is a number of electrons in the \( nl \)-shell. The exchange–correlation potential \( U_{\text{XC}}^{\text{LDA}}(r) \) is represented as a sum of the Slater exchange potential and a correlation potential:

\[ U_{\text{XC}}^{\text{LDA}}(r) = U_X(r) + U_C(r) = - \left( \frac{3}{\pi} \right)^{1/3} \rho^{1/3}(r) + U_C(r). \tag{5} \]

In the calculations, we used Perdew and Zunger parameterization of the correlation potential [31] which is presented in the form

\[ U_C(r_s) = \varepsilon_C(r_s) - \frac{1.229}{1 + 1.053 \sqrt{r_s}} + 0.444 r_s^{-1}, \tag{6} \]

\[ \varepsilon_C(r_s) = - 0.142 \left( 1 + 1.053 \sqrt{r_s} + 0.333 r_s^{-1} \right)^{-3/2}, \tag{7} \]

where \( r_s(r) = (4\pi \rho(r)/3)^{-1/3} \) is the local Wigner–Seitz radius for the electronic subsystem and \( \varepsilon_C(r_s) \) is the correlation energy per electron.

2.2. \textit{Ab initio} calculations

The \textit{ab initio} calculations were performed using the Gaussian 09 package [5]. For the description of the \( C_{60} \) and \( C_{20} \) fullerenes we used the split-valence triple-zeta basis set 6-311+G(d) with an additional set of polarization and diffuse functions. The systems were calculated by means of the density functional theory. To account for the exchange and correlation corrections, the Slater exchange functional [32] and the local Perdew functional (the so-called Perdew local, PL) [31] were used. By applying these rather simple functionals we wanted to achieve a full similarity in the description of the electronic subsystem within the jellium model and the \textit{ab initio} approaches.

The averaged electrostatic potential and the electron density over the directions of the position vector \( r \):

\[ \overline{U}_{\text{tot}}(r) = \overline{U}_n(r) + \overline{U}_d(r), \]

\[ \overline{U}_i(r) = \frac{1}{4\pi} \int U_i(r) \, d\Omega \quad (i = \text{tot, n, el}), \]

\[ \overline{\rho}(r) = \frac{1}{4\pi} \int \rho(r) \, d\Omega. \tag{9} \]

The averaged electron density includes only delocalized electrons, while the inner electron orbitals are excluded from the consideration.

3. Numerical results

In this section, we compare the results of the \textit{ab initio} and the jellium model calculations for \( C_{60} \) and \( C_{20} \). The fullerene \( C_{60} \) is discussed in detail below. The results for the \( C_{20} \) molecule and the comparison with \( C_{60} \) are discussed further in this section.

Using the methodology implemented in a number of papers [12, 16, 18, 21], we add a negative SW pseudopotential \( U_{\text{SW}} \) to the core potential (1):

\[ U_{\text{core}}(r) \rightarrow \left\{ \begin{array}{ll} U_{\text{core}}(r) + U_{\text{SW}}, & R_1 \leq r \leq R_2, \\
U_{\text{core}}(r), & \text{otherwise.} \end{array} \right. \tag{10} \]

The depth of the SW potential was chosen to obtain the same value of the outer-shell ionization potential as the defined one from the quantum-chemical calculation. The pseudopotential \( U_{\text{SW}} \) is shown by the dashed red curve in the lower panel of figure 3.

Single-electron energy spectra obtained from the \textit{ab initio} calculation and within the jellium model are presented in figure 1. For the ease of perception, the height of levels of the outer-shell ionization potential as the defined one from the quantum-chemical calculation. The pseudopotential \( U_{\text{SW}} \) is shown by the dashed red curve in the lower panel of figure 3.

Single-electron energy spectra obtained from the \textit{ab initio} calculation and within the jellium model are presented in figure 1. For the ease of perception, the height of levels of the outer-shell ionization potential as the defined one from the quantum-chemical calculation. The pseudopotential \( U_{\text{SW}} \) is shown by the dashed red curve in the lower panel of figure 3.
Figure 2. Radial electron density of \( \text{C}_6\text{O} \) obtained from the \textit{ab initio} calculation (solid black curve) and calculated by means of the jellium model: the standard one (dashed red curve), with the additional SW pseudopotential (solid red curve) and with the additional pseudopotential \( \Delta U \) (dash-dotted blue curve).

The radial density of the delocalized electrons obtained within the two approaches is presented in figure 2. It is shown that the standard jellium model without any corrections (dashed red curve) fails to represent the results of the \textit{ab initio} calculation (black curve). The additional SW pseudopotential does not modify the density distribution significantly (solid red curve).

As shown in figures 1 and 2, the jellium model with a simple additional pseudopotential represents neither the single-electron energy spectrum nor the electron density distribution. As opposed to more precise quantum chemistry methods, the jellium model does not take into account chemical features of the fullerene, such as hybridization of atomic orbitals in the formation of chemical bonding. However, the jellium model can be improved by means of a more sophisticated pseudopotential which will allow one to describe chemical properties of the real system. In this paper, we introduce the correction as a difference between the total electrostatic potential of the system obtained from the \textit{ab initio} calculation and the one obtained within the jellium model:

\[
\Delta U(r) = U_{\text{QC}}^{\text{tot}}(r) - U_{\text{jel}}^{\text{tot}}(r),
\]

where \( U_{\text{QC}}^{\text{tot}}(r) \) is defined by equation (8), and the potential \( U_{\text{jel}}^{\text{tot}}(r) \) obtained within the jellium model is defined as

\[
U_{\text{jel}}^{\text{tot}}(r) = U_{\text{core}}(r) + \int \frac{\rho(r')}{|r-r'|} \, dr'.
\]

The total potentials \( U_{\text{QC}}^{\text{tot}}(r) \) and \( U_{\text{jel}}^{\text{tot}}(r) \) of \( \text{C}_6\text{O} \) as well as their difference \( \Delta U(r) \) are shown in figure 3.

We note that previously several spiritually close averaged pseudopotentials have been introduced to correct the jellium model. For instance, it was done in the case of inhomogeneous electron gas on metal surfaces [34, 35] and for spherically symmetric metallic clusters [36, 37].

As opposed to the SW pseudopotential which affects equally all electrons of the system, \( \Delta U \) is an alternating-sign pseudopotential (see the lower panel of figure 3), therefore it is attractive in the vicinity of the fullerene ionic core and repulsive at larger distances from the fullerene surface. This means that such a potential affects differently the \( \sigma \)- and \( \pi \)-electrons of \( \text{C}_6\text{O} \) which are located on the surface of the molecule and perpendicularly to it, respectively. Therefore, one can conclude that by means of such a potential it is possible to account, to some extent, for the hybridization properties of the fullerene.

The single-electron energy spectrum obtained within the ‘modified’ jellium model with \( \Delta U \) taken as an additional pseudopotential is presented in figure 4. The modification allows one to obtain a better agreement of the jellium calculation with the \textit{ab initio} one for the inner single-node \( 2s \cdots 5f \) orbitals. On the contrary, it shifts the 6g and 7h ionization potentials by 2.8 and 2.5 eV, respectively and still does not lead to a better quantitative agreement for the whole spectrum (see figure 4).
Figure 4. Single-electron energy levels of C$_{60}$ obtained from the \textit{ab initio} calculation (empty and filled squares) and within the modified jellium model with an additional pseudopotential $\Delta U$ (empty and filled triangles). Nodeless $\sigma$-orbitals and single-node $\pi$-orbitals are labelled by empty and filled symbols, respectively.

Figure 5. The additional pseudopotential $\Delta U$ in cases of C$_{60}$ (solid curve) and C$_{20}$ (dashed curve).

Introduction of the alternating-sign pseudopotential $\Delta U$ allows one to improve significantly the electron density distribution (see the dash-dotted blue curve in figure 2). The difference between the \textit{ab initio} calculated electron density and the one from the jellium model calculation in the spatial region 8–12 au may contribute to the shift of 6g and 7h ionization potentials (see figure 4).

Below we present and discuss the results for the C$_{20}$ molecule. Following the formalism described above for C$_{60}$, the additional pseudopotential $\Delta U$ is introduced as a difference between the total electrostatic potential of C$_{20}$ obtained from the \textit{ab initio} quantum-chemical calculation and the one obtained within the jellium model. Figure 5 represents the correction $\Delta U$ calculated for C$_{60}$ and C$_{20}$. It is shown that $\Delta U$ has a similar alternating-sign shape for both molecules but it is more asymmetric in the case of C$_{20}$.

The single-electron energy spectra of C$_{20}$ are presented in figure 6. The pseudopotential $\Delta U$ does not influence significantly all nodeless orbitals while the single-node orbitals are shifted. This shift leads to a better agreement of the \textit{ab initio} and jellium calculations for 2s and 3p shells but gives a wrong value for the outer 4d and 5f ionization potentials.

The additional pseudopotential $\Delta U$ exerts a similar influence on the electron density distribution of C$_{20}$, as in the case of C$_{60}$ (see figure 7). In comparison with a standard jellium model (dashed red curve), the modified one improves the density distribution in the vicinity of the fullerene core (dash-dotted blue curve) but the electron density is spread partly to the spatial region 5–9 au.

Having considered two different fullerenes within the spherical jellium model, one can conclude that the precise description of single-electron energy spectra of these systems by means of the jellium model is a very difficult and elusive task, though such an approach produces mostly the right sequence of energy levels. Additional pseudopotentials allow one to obtain the right value of the ionization potential only for several outer shells but do not alter the overall situation significantly. At the same time, we suppose that by improving the ground-state density distribution with the
Figure 7. Radial electron density of C_{20} obtained from the \textit{ab initio} calculation (solid curve) and calculated within the jellium model, the standard one (dashed curve) and with the additional pseudopotential $\Delta U$ (dash-dotted curve).

Figure 8. Pseudopotential $\Delta U$ for the C_{60} (upper panel) and C_{20} (lower panel) compounds. The initial curve is presented by the thick solid (black) line, the dashed (red) line represents the fitting curve constructed as a sum of three primitive Lorentz functions (thin blue lines).

introduced pseudopotential one can achieve higher accuracy while constructing the photoionization amplitudes.

The obtained pseudopotentials for C_{60} and C_{20} can be well fitted by three Lorentz functions. The result of the fitting procedure is presented in figure 8. Supposing $\Delta U(r) \equiv y(x)$, the resulting fitting function could be defined in the following form:

$$y(x) = y_0 + \sum_{i=1}^{3} \frac{2A_i}{\pi} \frac{w_i}{4(x - x_i)^2 + w_i^2},$$

(13)

where $y_0$ is the offset constant, $x_i$ is the position of the peak maximum, $w$ is the full-width at half-maximum and $A$ is the normalization factor. The obtained values of these parameters are presented in table 1.

As was shown above, the pseudopotential $\Delta U$ has a more asymmetric form in the case of C_{20} than in the case of C_{60}; therefore, it should affect differently the $\pi$-electrons of these systems. Figure 9 represents the radial density of $\pi$-electrons in the C_{60} and C_{20} molecules obtained within the standard jellium model as well as the one augmented by $\Delta U$. The minimum of the $\pi$-electron density distribution is located at 6.78 au for C_{60} and 4.03 au for C_{20}. These values are slightly shifted from the mean radius of the molecules, which equals 6.67 and 3.86 au, respectively. It is shown that due to the hybridization-related correction $\Delta U$, $\pi$-electrons in both systems are distributed non-uniformly in the inner and outer regions of the molecules.

To estimate a relative degree of spill-out of the $\pi$-electrons to the outer region of the fullerene molecules, we normalized the density distributions by dividing them by the number of
4. Conclusion

To conclude, we have introduced a new type of correction for the description of the fullerene C_{60} and C_{20} within the spherically symmetric jellium model. The correction is represented as an additional pseudopotential which originates from the difference between the precise ab initio calculation and the one within the jellium model. Due to the alternating-sign shape of the potential, it affects the \sigma- \text{ and } \pi- \text{electrons of the system differently. Therefore, this potential allows one to mimic partially the sp^2-hybridization, which occurs in formation of fullerene, and, thus, to import the hybridization effects into the standard jellium model. We have shown that the correction used improves significantly the electron density distribution as compared to the standard jellium model and the one with an additional square-well pseudopotential. Like the other previously used corrections, it does not allow one to obtain a quantitative agreement with an \textit{ab initio} calculation for the single-electron energy spectrum but reproduces the sequence of energy levels corresponding to the one following from the more precise quantum-chemical calculation.

As the next step of this work, the correction to the jellium model, introduced in this paper, will be utilized further for the calculation of the dynamic response of fullerene in the processes of photon and electron impact excitation. We suppose that improving the ground-state density distribution with the introduced pseudopotential it is possible to get an accurate description of the excitation processes of fullerene. Particular attention will be paid on the study of collective electron excitations. This work is currently in progress and the results will be presented elsewhere. An implementation of the presented formalism for larger fullerene molecules, nanotubes etc could be another topic of further investigations.

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References

[1] Kroto H W \textit{et al} 1985 \textit{Nature} 318 162
[2] Sattler K D 2010 Handbook of Nanophysics: Clusters and Fullerenes (Boca Raton, FL: CRC Press)
[3] Mroz P \textit{et al} 2008 \textit{Medicinal Chemistry and Pharmacological Potential of Fullerenes and Carbon Nanotubes} vol 1 ed F Cataldo and T Da Ros (New York: Springer) p 79
[4] Solov'yov A V 2005 Int. J. Mod. Phys. B 19 4143
[5] Frisch M J \textit{et al} 2009 Gaussian 09 Revision A.1, Gaussian Inc. Wallingford CT
[6] Kaplan I G 1997 Z. Phys. D 40 375
[7] Rubio A, Alonso J A, Blase X, Balbas L C and Louie S G 1996 \textit{Phys. Rev. Lett.} 77 247
[8] Solov'yov A V, Ipatov A N and Zhyzhin M L 2011 \textit{Phys. Rev. Lett.} 107 183401
[9] Ekardt W 1984 \textit{Phys. Rev. B} 30 1558
[10] Kharchenko V A, Ivanov V K, Ipatov A N and Zhyzhin M L 1994 \textit{Phys. Rev. A} 50 1459
[11] Polozkov R G, Ivanov V K, Verkhovtsev A V and Solov’yov A V 2009 \textit{Phys. Rev. A} 79 063203
[12] Yannouleas C and Landman U 1994 \textit{Chem. Phys. Lett.} 217 175
[13] Yabana K and Bertsch G F 1993 \textit{Phys. Scr.} 48 633
[14] Guet C and Johnson W R 1992 \textit{Phys. Rev. B} 45 1283
[15] Jäntäli A, Tchaplyguine M, Mikkelä M-H, Björnholm O and Huttula M 2011 \textit{Phys. Rev. Lett.} 107 183401
[16] Puska M J and Nieminen R M 1993 Phys. Rev. A 47 1181
[17] Wendin G and Wästberg B 1993 Phys. Rev. B 48 14764
[18] Rüdel A, Hentges R, Becker U, Chakraborty H S, Madjet M E and Rost J-M 2002 Phys. Rev. Lett. 89 125503
[19] Kidun O, Fominikh N and Berakdar J 2004 J. Phys. B: At. Mol. Opt. Phys. 37 L321
[20] Polozkov R G, Ivanov V K and Solov'yov A V 2005 J. Phys. B: At. Mol. Opt. Phys. 38 4341
[21] Madjet M E, Chakraborty H S, Rost J-M and Manson S T 2008 J. Phys. B: At. Mol. Opt. Phys. 41 105101
[22] Pavlyukh Y and Berakdar J 2010 Phys. Rev. A 81 042515
[23] Prinzbach H et al 2000 Nature 407 60
[24] Zhang Q L et al 1986 J. Phys. Chem. 90 525
[25] Krätzschmer W, Fostiropoulos K and Huffman D R 1990 Chem. Phys. Lett. 170 167
[26] Goroff N S 1996 Acc. Chem. Res. 29 77
[27] Martins J L, Troullier N and Weaver J H 1991 Chem. Phys. Lett. 180 457
[28] Haddon R C, Brus L E and Raghavachari K 1986 Chem. Phys. Lett. 125 459
[29] Östling D, Apell P and Rosen A 1993 Europhys. Lett. 21 539
[30] Gianturco F A, Kashenock G Yu, Lucchese R R and Sanna N 2002 J. Chem. Phys. 116 2811
[31] Perdew J P and Zunger A 1980 Phys. Rev. B 23 5048
[32] Kohn W and Sham L J 1965 Phys. Rev. 140 A1133
[33] Lu T and Chen F 2012 J. Comput. Chem. 33 580
[34] Lang N D and Kohn W 1970 Phys. Rev. B 1 4555
[35] Perdew J P and Monnier R 1976 Phys. Rev. Lett. 37 1286
[36] Alasia F, Serra L, Broglia R A, Van Giai N, Lipparrini E and Roman H E 1995 Phys. Rev. B 52 8488
[37] Vieira A, Begoña Torres M, Fiolhais C and Carlos Balbás L 1997 J. Phys. B: At. Mol. Opt. Phys. 30 3583