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Towards efficient *ab initio* calculations of electron scattering by polyatomic molecules. III. Modelling correlation-polarization interactions

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Abstract. We explore an implementation of correlation-polarization interactions for electrons scattering by polyatomic molecules. The short-range correlation is approximated by local and non-local DFT models commonly used in quantum chemistry and solid state physics. The long-range polarization is represented by general full tensor components. Furthermore, we propose a robust and stable technique to calculate momentum-space matrix elements of such a composite potential. The quality of several selected DFT potentials is tested by elastic scattering calculations for a class of small hydrocarbon molecules represented by propane and cyclopropane.

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1. Introduction

Modification of the static-exchange potential (outlined in the following section) by a local form of interaction accounting for correlation and even polarization of the target's bound orbitals is not a new idea. The first models used the long-range asymptotic form $V_p = -\alpha_0/2r^4$ with a short-range cutoff function in order to remove the singular behavior at the origin (Morrison and Collins 1978). A single parameter of this model, the cutoff radius, was then determined by adjusting the calculated cross sections to some well-established feature of the results. For modelling the short-range correlation between the scattered electron and the target electron density, use of the density functional theory (DFT) was proposed (O'Connell and Lane 1983, Padial and Norcross 1984). They employed a local spin density (LSD) approximations emerging from the field of solid-state physics (Vosko *et al* 1980, Perdew and Zunger 1981, both later refined by Perdew and Wang 1992). All these forms of the LSD correlation are based on Green's-function Monte Carlo simulation for electrons in a finite volume, subject to periodic boundary conditions. The correlation energy per electron was then extrapolated to infinite volume (Ceperley and Alder 1980). The practical accuracy of all these LSD approximations is similar and they are a core component of all modern DFT functionals used in quantum chemistry. They are often referred to as LDA (local density approximation) in the literature of electron-molecule collisions.

A further way to improve LSD approximation came in a form of a generalized gradient approximation (GGA) by Perdew *et al* 1992 (the functional is referred in the literature as PW91). A different way to incorporate the density gradient corrections was used by Lee, Yang and Parr 1988, who turned the correlation-energy formula of Colle and Salvetti 1975 into a DFT functional form by use of the first and second gradients of electron density (LYP functional).

Development of DFT correlation functionals was accompanied by a simultaneous development of the exchange functionals. Although a Hartree-Fock exchange energy, in principle exact, is computationally cheap, most of the successful exchange-correlation functionals (PBE0, B3LYP, etc.) contain a weighted mixture of the Hartree-Fock exchange and gradient corrected exchange functionals. For example, PBE0 contains 75% of exchange functional constructed by Perdew, Burke and Ernzerhof 1996. Another highly accurate, gradient corrected functional is from Becke 1988, which takes 80% of the exchange energy present in the B3LYP exchange-correlation functional. Both exchange-correlation functionals have been successfully applied to vast number of molecular systems during the last decade.

We feel that despite the intense development of DFT in solid-state physics and bound-state quantum chemistry, its adaptation for modelling the electron-molecule collisions has been rather slow. One reason may be lack of Hohenberg-Kohn theorem for a continuum (N+1)-electron state describing the scattering event. Therefore many authors employed the DFT correlation potential generated by a closed-shell ground-state density of the target with the density of the continuum orbital excluded. Even with

such a minor conceptual discrepancy the addition of a simple LDA correlation potential resulted in calculated cross section being in better agreement with experimental data (among many examples we chose Gianturco and Rodriguez-Ruiz 1993, Čurík and Gianturco 2002a, Telega *et al* 2004, Tonzani and Greene 2005)

Motivated by the success of the LDA exchange and correlation functionals in the electron-molecule computational modelling, here we explore the possibility of their implementation in a framework of Discrete Momentum Representation (DMR) method. Previously Čurík *et al* 2008 employed LDA correlation in the DMR method for calculations of vibrationally inelastic collisions of electrons with methane molecules. The spherically symmetric case is extended in the Section 3 to a general asymptotic polarization represented by a polarizability tensor. For the short-range parts of the correlation interaction we make use of several DFT functionals commonly used in quantum chemistry. Their quality is assessed in Section 4 for propane and cyclopropane molecules.

2. Optical potential

Discrete momentum representation (DMR) method belongs to the class of one-electron methods that make use of an optical potential. The method calculates elastic body-frame scattering amplitudes by solving one-electron Lippmann-Schwinger equation (Polášek *et al* 2000, Čurík and Čársky 2003)

$$\langle \mathbf{k}_o | T | \mathbf{k}_i \rangle = \langle \mathbf{k}_o | V | \mathbf{k}_i \rangle + \int d^3\mathbf{k} \frac{\langle \mathbf{k}_o | V | \mathbf{k} \rangle \langle \mathbf{k} | T | \mathbf{k}_i \rangle}{k_0^2 - k^2 + i\epsilon}, \quad (1)$$

where $\mathbf{k}_i$ and $\mathbf{k}_o$ are momenta of the incoming and outgoing electrons, respectively. Optical potential describing an interaction between the scattered electron and the target molecule is denoted by V . Collision energy E is defined as $E = k_0^2/2$. After some careful treatment of the singular kernel in the above equation one can discretize the integral on r.h.s. of (1) as shown in a greater detail in the Part I of this series (Čársky 2010a). This technique leads to a set of linear algebraic equation that can be solved by a matrix inversion (Čurík and Čársky 2003). The optical potential used in DMR method has been recently extended and now it contains static, exchange and correlation-polarization contributions (Čurík *et al* 2008)

$$V = V_s + V_x + V_{cp}. \quad (2)$$

The static V_s contribution to the optical potential (2) is obtained from a set of N doubly-occupied Hartree-Fock orbitals $\varphi_i(\mathbf{r})$ of the closed-shell target as

$$\langle \mathbf{r} | V_s | f \rangle = 2 \sum_i^N \int d^3\mathbf{r}' \frac{|\varphi_i(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} f(\mathbf{r}) - \sum_j \frac{Z_j}{|\mathbf{r} - \mathbf{R}_j|} f(\mathbf{r}). \quad (3)$$

The first term in this equation describes a repulsion with the electronic charge density, while the second term corresponds to an attraction to the molecular nuclei positioned

at $\mathbf{R}_j$. Similarly, acting of the exchange interaction on the continuum function f can be written as

$$\langle \mathbf{r} | V_x | f \rangle = - \sum_i^N \int d^3\mathbf{r}' \frac{\varphi_i(\mathbf{r}') f(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \varphi_i(\mathbf{r}) . \quad (4)$$

The sum $V_s + V_x$ is *exact static-exchange* approximation in the literature of electron-molecule collisions and it has been employed by many authors to successfully describe the interaction of continuum electron with a target molecular system. For extensive reviews see Huo and Gianturco 1995 (p. 79), Lane 1980 (p. 47).

As can be seen from Eq. (1) the DMR method requires momentum-space representation of the optical potential. The local parts V_s and V_{cp} are then obtained by Fourier transform integrals, while the nonlocal exchange contribution is more computationally demanding. Its efficient implementation via interpolation of complex Shavitt functions is described in the Part II of this series (Čársky 2010b).

3. Correlation and polarization interaction

The short-range correlation potential is obtained by the DFT models mentioned in Section 1. We have chosen to examine three correlation functionals that are widely used and known in quantum chemistry calculations. The first is the LDA correlation potential of Perdew and Wang 1992, although the alternative choices due to Vosko *et al* 1980 or Perdew and Zunger 1981 lead to the same results. Gradient corrections to this potential are then applied with GGA potential of Perdew *et al* 1992 (PW91 potential) and independently we also employ the gradient corrections of Lee, Yang and Parr 1988 (LYP functional).

It is appropriate to address the confusing vocabulary used in two different fields of quantum calculations. In the literature of solid-state physics and quantum chemistry the gradient corrected functionals are referred as non-local as they gather information of the electron density surrounding a point of interest. It is achieved via terms with first and second gradients of the electron density that enter the functional. However, from the strict point of view of quantum mechanics, the corresponding potentials are local as they simply multiply the wave function in the Schrödinger equation.

All the three correlation potentials that we explore decrease exponentially outside the molecule following the exponential decay of the bound electron density. This defect in DFT was noted long time ago (Umrigar and Gonze 1994, Almbladh and von Barth 1985). Such an incorrect long-range behavior of the DFT potentials causes many problems in description of induced moments of delocalized charge densities. Accordingly, special treatment has been undertaken in calculations of charge-transfers (Dreuw and Head-Gordon 2004) or dispersion forces (Antony and Grimme 2006, Zhao and Truhlar 2007). Rigorously, the long-range correlation potential should be taken as (Almbladh

and von Barth 1985, Umrigar and Gonze 1994)

$$V_p(\mathbf{r}) = -\frac{1}{2r^6} \sum_{i,j}^3 \alpha_{ij} x_i x_j, \quad (5)$$

where the symmetric 3x3 matrix α_{ij} is a polarizability tensor and $r^2 = x_1^2 + x_2^2 + x_3^2$. Therefore, guided by the previous works of Padial and Norcross 1984 or Telega *et al* 2004, we connect the correct long-range term V_p of the correlation interaction (5) with the short-range term V_c described by one of the DFT correlation potentials. Since our technique of such a connection differs from the above mentioned procedures, we describe it in more detail.

A smooth connection of a general and anisotropic asymptotic form (5) to a short-range anisotropic potential is not uniquely defined. Telega *et al* 2004 suggest finding a crossing point r_c of a spherically symmetric components of the long- and short-range parts. Of course r_c is not a proper crossing point of the higher partial-wave components. Overall smoothness is then achieved by adding the higher-order induced multipoles leading to a modification of the asymptotic form (5) where faster decaying terms are added. In our approach we prefer to keep the asymptotic form (5) and perform the smooth connection for each of the partial waves that come into play. As the first step, we expand the general tensor form (5) into partial waves

$$V_p(\mathbf{r}) = \sum_{l=0}^2 \sum_{m=-l}^l v_l^m(r) S_l^m(\hat{\mathbf{r}}), \quad (6)$$

where $S_l^m(\hat{\mathbf{r}})$ are normalized real spherical harmonics

$$S_l^m(\vartheta, \varphi) = \left[\frac{2l+1}{2\pi(1+\delta_{0m})} \frac{(l-m)!}{(l+m)!} \right]^{\frac{1}{2}} P_l^m(\cos \vartheta) \begin{cases} \cos m\varphi, & m \geq 0 \\ \sin m\varphi, & m < 0 \end{cases}. \quad (7)$$

The radial functions $v_l^m(r)$ of the Eq.(6) can be obtained analytically as

$$v_l^m(r) = -\frac{\alpha_l^m}{2r^4}, \quad (8)$$

where α_l^m are the irreducible components of the Cartesian tensor of rank 2 (Weissbluth 1978, p.174)

$$\begin{aligned} \alpha_0^0 &= \frac{\sqrt{4\pi}}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \\ \alpha_1^0 &= \alpha_1^{-1} = 0 \\ \alpha_2^0 &= \sqrt{\frac{4\pi}{5}} \left(\alpha_{zz} - \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \right) \\ \alpha_2^1 &= -2\sqrt{\frac{4\pi}{15}} \alpha_{xz} \\ \alpha_2^{-1} &= -2\sqrt{\frac{4\pi}{15}} \alpha_{yz} \\ \alpha_2^2 &= 2\sqrt{\frac{4\pi}{15}} \frac{\alpha_{xx} - \alpha_{yy}}{2} \\ \alpha_2^{-2} &= 2\sqrt{\frac{4\pi}{15}} \alpha_{xy} \end{aligned} \quad (9)$$

For the short-range part V_c we separate the interaction into two orthogonal angular subspaces:

$$V_c(\mathbf{r}) = \sum_{l=0}^2 \sum_{m=-l}^l w_l^m(r) S_l^m(\hat{\mathbf{r}}) + W_0(\mathbf{r}) . \quad (10)$$

All the terms on the left and right side of Eq. (10) decay exponentially. Because the DFT form of the short-range correlation potential $V_c(\mathbf{r})$ is numerical the radial functions $w_l^m(r)$ are obtained by a numerical angular projection. It follows that $W_0(\mathbf{r})$ contains only partial components with $l > 2$.

Having both (short- and long-range) interactions split into the partial waves the connection procedure is readily available. We connect each partial wave of $v_l^m(r)$ and $w_l^m(r)$ independently up to $l = 2$ forming 6 crossing points R_l^m . Three short-range functions $w_l^m(r)$ with $l = 1$ decay exponentially as they don't have the long-range counterparts $v_l^m(r)$ to connect to. It is a consequence of a symmetry of the polarizability tensor. Therefore, we can define the connected radial functions

$$u_l^m(r) = \begin{cases} w_l^m(r) & \text{for } r < R_l^m \\ v_l^m(r) & \text{for } r \geq R_l^m \end{cases} . \quad (11)$$

The total correlation-polarization potential V_{cp} is then evaluated by the following formula

$$V_{cp}(\mathbf{r}) = \sum_{l=0}^2 \sum_{m=-l}^l u_l^m(r) S_l^m(\hat{\mathbf{r}}) + W_0(\mathbf{r}) . \quad (12)$$

The above procedure exploited the simple fact the asymptotic polarization potential V_p is fully contained in the angular space defined by $l = 0$ and $l = 2$. Hence, we made sure the connection between the short- and long-range parts is smooth in every partial component up to $l = 2$. All the higher components of the resulting potential V_{cp} then decay exponentially.

The final step needed to obtain the momentum-space matrix elements entering the Lippmann-Schwinger equation (1) is a Fourier transform (FT) integral

$$\langle \mathbf{k}_1 | V_{cp} | \mathbf{k}_2 \rangle = \frac{1}{(2\pi)^3} \int d^3\mathbf{r} V_{cp}(\mathbf{r}) e^{i(\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{r}} . \quad (13)$$

The integral in the equation above is typically solved by a discrete fast Fourier transform (FFT) method. This is achieved by bounding the integral in a three-dimensional rectangular volume and by evaluating the argument on a three-dimensional rectangular grid. In our implementation we used a cubic volume. We observed a cube size of several hundreds bohrs is needed in order to achieve a sufficient accuracy of the resulting integrals for the small $\mathbf{k}_2 - \mathbf{k}_1$ vectors. The cause of the slow size convergence is the long-range nature (5) of the V_{cp} potential. However, with such a large integration volume it becomes difficult to sample the potential with a sufficient density in the area of the molecule, where the V_{cp} changes rapidly.

In order to solve this dilemma we subtract and add a well-behaved analytical function that cancels the V_{cp} potential at the long range. We also require this function to have an analytical FT form:

$$V_{cp} = \underbrace{\left[V_{cp} + \frac{1}{2(r^6 + a^6)} \sum_{i,j}^3 \alpha_{ij} x_i x_j \right]}_{\text{numerical FFT } V_{cp}^n} - \underbrace{\frac{1}{2(r^6 + a^6)} \sum_{i,j}^3 \alpha_{ij} x_i x_j}_{\text{analytical FT } V_{cp}^a} . \quad (14)$$

The parameter a is chosen to be sufficiently small in order to achieve the long-range cancellation in the V_{cp}^n term. However, if the cutoff a is chosen too small it may produce a rapidly changing behavior at the origin. To compromise we have found the procedure very robust and accurate for a being anywhere between 5% and 15% of the FFT cube size. Evaluation of the FT integral for the V_{cp}^a term is described in the Appendix A. Here we present only the final results:

$$\frac{1}{(2\pi)^3} \sum_{i,j}^3 \alpha_{ij} \int d^3 \mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} \frac{x_i x_j}{2(r^6 + a^6)} = \frac{1}{(2\pi)^3} \sum_{ij}^3 \alpha_{ij} G_{ij}(\mathbf{k}) , \quad (15)$$

with

$$G_{ij}(\mathbf{k}) = \frac{F'(k)}{k} \delta_{ij} + \left[\frac{F''(k)}{k^2} - \frac{F'(k)}{k^3} \right] k_i k_j , \quad (16)$$

and

$$F(k) = -\frac{\pi^2}{3a^4 k} e^{-ka/2} \left[e^{-ka/2} + \sqrt{3} \sin(ka \frac{\sqrt{3}}{2}) - \cos(ka \frac{\sqrt{3}}{2}) \right] . \quad (17)$$

For practical implementation one also needs the limit at the origin

$$\lim_{\mathbf{k} \rightarrow 0} G_{ij}(\mathbf{k}) = \frac{2\pi^2}{9a} . \quad (18)$$

4. Application to elastic scattering on small hydrocarbons

In order to test the current implementation of correlation-polarization forces within the DMR method we have selected two similar molecular systems, namely cyclopropane and propane molecules. Both molecules have been intensively studied experimentally (Allan 1994, Allan and Andric 1996, Szmytkowski *et al* 2002a,2002b, Makochekanwa *et al* 2006, Boesten *et al* 1994, Tanaka *et al* 1999). While number of theoretical calculations is thorough for the cyclopropane molecule (Winstead *et al* 1992, Beyer *et al* 1997, Čurík and Gianturco 2002a,2002b, Makochekanwa *et al* 2006), to our knowledge there is only one SE calculation by Winstead *et al* 1991 for the propane molecule.

A visual comparison of the spherical components $u_0^0(r)$ defined by Eq. (11) is displayed in Fig. 1 for both studied polyatomic molecules. The general features of the correlation potentials are as expected. The cyclic C_3H_6 exhibits slightly stronger correlation in the core area of the molecule while the open ring of C_3H_8 allows stronger correlation in the low-density outskirt regions of the molecule resulting in a stronger

Figure 1. Visual comparison of different correlation functionals used in the present study. For simplicity only the dominant spherical components $u_0^0(r)$ of Eqs. (11,12) are displayed. Left panel shows the data for the cyclopropane molecule, right panel for the propane molecule.

asymptotic polarizability. As far as the differences among different functionals go, the LYP gradient correction to the LDA potential results in a stronger correlation especially on the peripheral low-density region. This feature is valid for both presented molecules and it extends even for more unpublished results of polyatomic molecules. On the other hand a behavior for the PBE potential is not as predictable in the low-density region, as seen for C_3H_6 and C_3H_8 in Fig. 1. All the calculated correlation potentials smoothly connect to the asymptotic form (5). Polarizability tensor components used in the present calculations were obtained as linear response functions in Kohn-Sham DFT (Rinkevicius *et al* 2003) calculations with B3LYP hybrid functional and Sadlej's polarized VTZ basis sets (Sadlej 1993) as implemented in program Dalton Release 2.0 (2005). Body frame of reference was chosen by principal axes, thus the calculated polarizability tensors are diagonal:

$$\boldsymbol{\alpha}(C_3H_6) = \begin{pmatrix} 38.8 & & \\ & 38.8 & \\ & & 33.8 \end{pmatrix}, \quad \boldsymbol{\alpha}(C_3H_8) = \begin{pmatrix} 38.0 & & \\ & 45.6 & \\ & & 40.2 \end{pmatrix}.$$

Both tensors compare favorably with an experimental data for spherical polarizabilities $\alpha_0(C_3H_6) = 38.2$ a.u. (Krishtenko *et al* 1998) and $\alpha_0(C_3H_8) = 42.5$ a.u. (Lide 1994).

Parameters for the numerical quadrature of the integral on r.h.s. of Eq. (1) are taken, for these two molecules, from Table 1 in the Part I of this series (Čársky 2010a). Calculated fixed-nuclei integral cross sections for all the present correlation-polarization models applied to the cyclopropane molecule are displayed in Fig. 2. It is clear that the presence of the correlation-polarization interaction leads to some major changes in the magnitude and shape of the cross sections below 10 eV. Moreover, we found the differences among all the three correlation models fairly minor and therefore we chose

Figure 2. The elastic integral cross sections for electron scattering by cyclopropane molecules. Left panel compares results of various correlation models with available experimental data. The right panel shows comparison of available calculations.

the LYP model as their representative in the following discussion. The right panel of Fig. 2 shows a comparison of the available theoretical predictions for the elastic integral cross section. Our calculations are in a very good agreement with the calculations of Čurík *et al* 2002a as a result of very similar interaction models. Čurík *et al* 2002a used a non-local separable approximation of the exchange part to be compared to the present exact exchange model. Previous work employed the LDA short-range functional smoothly connected to the spherical polarization potential, however all the polarization tensor components are used in the present calculations. These small differences between the two models may explain pronounced structure around 6 eV visible in the present results. The structure was identified by Čurík *et al* 2002b and Allan and Adric 1996 as A'_2 shape resonance leading to a selective vibrational excitation of C-C ring stretching mode. Fixed-nuclei calculations of Makochekanwa *et al* 2006 and Beyer *et al* 1997 predict lower integral cross section than the SEP results discussed above. However, they both predict the presence of the A'_2 shape resonance at 6.2 eV and 5.4 eV, respectively.

The elastic differential cross sections (DCS's) of electrons scattered by cyclopropane are displayed in Fig. 3. The agreement of the present ESE+LYP model with the experimental angular distributions is again very good at both collision energies: 5 eV (left panel) and 10 eV (right panel). In comparison to the experimental data at 10 eV, present calculations predict slightly higher cross section at small and large scattering angles. This difference, especially at angles above 140° , may lead to a different experimental extrapolation of the DCS, consequently resulting in a smaller integral cross section visible in Fig. 2.

In order to make a full use of our tensor description of the asymptotic polarization, we selected a molecular system with a smaller symmetry yet of similar size as our second testing case: the propane molecule. Figure 4 summarizes the available experimental and theoretical data for elastic collisions of electrons with the propane molecules. The

Figure 3. Elastic differential cross sections for electron scattering by cyclopropane molecules. The left panel shows data for the collision energy of 5 eV while the right panel is for 10 eV. The data of Čurík and Gianturco 2002 and Allan 1994 are shown on the left panel for the collision energy 5.5 eV.

Figure 4. Elastic integral cross sections for electron scattering by propane molecules. Left panel compares results of various correlation models with available experimental data. Right panel shows present results with the LYP functional and the previous SE calculations of Winstead *et al* 1991.

left panel compares our correlation models with the measurements of Szmytkowski *et al* 2002, Tanaka *et al* 1999 and Boesten *et al* 1994. The experimental cross sections exhibit a strong maximum around 8 eV. Again the presence of the correlation-polarization forces in our model strongly affects the value of our calculated integral cross section below the collision energy of 12 eV. The difference among correlation models is more visible for this system, as seen in Fig. 1. The strongest correlation provided by the LYP functional shifts the peak in the integral cross section down to 8.5 eV while the PBE and LDA functionals point to 9.5 eV. The right panel of Fig. 4 also shows the SE calculations of Winstead *et al* 1991 that are similar to present ESE results (the left panel of the Fig. 4).

Figure 5. Elastic differential cross sections for electron scattering by propane molecules. We compare our LYP calculations (full curve) with experimental data of Boesten *et al* 1994 (diamonds) and Tanaka *et al* 1999 (crosses). Broken curve represents the SE calculations Winstead *et al* 1991.

In order to complete our comparisons we likewise present the angular distributions for the propane molecule in Fig. 5. The agreement between our calculated results and the experimental data is very good for 5 eV (left panel) while for 10 eV we observe behavior similar to the case of cyclopropane molecule. Our predicted differential cross sections are slightly higher for the small and large scattering angles resulting in larger integral cross section shown in Fig. 4.

5. Conclusions

The present study has several goals: first to extend previously published spherical polarization model in the DMR method (Čurík *et al* 2008) to a form of the general polarizability tensor; second, to implement and discuss several correlation potentials commonly used in the DFT community and codes (the LDA, PBE and LYP potentials); third, to test the reliability of the constructed potentials on two simple hydrocarbon molecules, propane and cyclopropane.

Regarding the second and third objectives, the reliability of the potentials are gauged by their agreement with experimental data. In the case of the cyclopropane molecule, all three correlation models led to very similar results. Elastic integral cross sections presented in this paper agree very well with calculations by Čurík and Gianturco 2002b and total cross sections measurements of Szmytkowski *et al* 2002. Experimental and theoretical integral cross sections of Makochekanwa *et al* 2006 are distinctly lower. However, in terms of angular distributions, the present calculations agree very well with the experimental data suggesting the difference between our integral cross sections and cross-beam integral cross sections might rest in the extrapolation of the cross-beam data to large scattering angles. Similar conclusions can be drawn in the case of propane

molecule with a one distinct difference. The stronger LYP correlation model performs considerably better than the LDA and PBE correlation potentials.

In order to draw some general conclusions about the quality of the correlation models in the electron molecule collisions, many more molecular systems should be studied. Computationally, presented implementation of correlation potentials is very efficient and can be applied to molecules larger than propane and cyclopropane. We hope to provide some data to this open issue in the near future using the methods and model presented in this paper.

Appendix A. Fourier transform of the full tensor asymptotic potential

The aim of the appendix is to evaluate the following Fourier transform integrals

$$G_{ij}(k) = \int d^3\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \frac{x_i x_j}{2(r^6 + a^6)} . \quad (\text{A.1})$$

As a first step we define the Fourier transform $F(k)$ of the radial component of the potential. The angular part is then integrated out with the only radial integral remaining:

$$F(k) = - \int d^3\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \frac{1}{2(r^6 + a^6)} = -\frac{2\pi}{k} \int_0^\infty dr \frac{r \sin kr}{r^6 + a^6} . \quad (\text{A.2})$$

The radial integral can be transformed to a contour integral in the complex plane as follows

$$\int_0^\infty dr \frac{r \sin kr}{r^6 + a^6} = \frac{1}{2} \int_{-\infty}^\infty dr \frac{r \sin kr}{r^6 + a^6} = \frac{1}{2} \text{Im} \int_C dz \frac{ze^{ikz}}{z^6 + a^6} , \quad (\text{A.3})$$

with the contour C shown in the Figure A1. There are three residual points in the upper complex plane that count for the residue theorem:

$$\begin{aligned} z_1 &= ae^{i\pi/6} , \\ z_2 &= ia , \\ z_3 &= ae^{i5\pi/6} . \end{aligned} \quad (\text{A.4})$$

By employing the residue theorem for the last integral in (A.3) we obtain the radial Fourier transform $F(k)$ defined in the Eq. (A.2) as follows:

$$F(k) = -\frac{\pi^2}{3a^4k} e^{-ka/2} \left[e^{-ka/2} + \sqrt{3} \sin\left(ka \frac{\sqrt{3}}{2}\right) - \cos\left(ka \frac{\sqrt{3}}{2}\right) \right] . \quad (\text{A.5})$$

Figure A1. Contour integration path used in the Eq. (A.3) together with the three residual points in the upper plane

By comparing equations (A.1) and (A.2), one can easily see the general tensor components $G_{ij}(\mathbf{k})$ may be obtained by partial derivatives of the radial function $F(k)$

$$G_{ij}(\mathbf{k}) = \frac{\partial^2}{\partial k_i \partial k_j} F(k) . \quad (\text{A.6})$$

The second-order partial derivatives directly lead to the Eq. (16).

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