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Cubic-grid Gaussian basis sets for electron scattering calculations IV.

Differential cross-section averaging for isotropic samples

Vojtěch Hrouda[1], Martin Polášek[1], Petr Čársky[1], Josef Michl[2]

[1] J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic

[2] Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, CO 80309-0215, USA

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Summary. An analytical formula has been derived for averaging the differential cross section for electron scattering with respect to isotropic target molecule orientation. It may be applied to any type of T-matrix element $\langle \boldsymbol{k}^{\text{out}} | T | \boldsymbol{k}^{\text{in}} \rangle$ in which the plane-wave functions $\boldsymbol{k}^{\text{out}}$ and $\boldsymbol{k}^{\text{in}}$ are expanded in a set of s-type Gaussian functions. The formula for averaging was tested against results obtained by Monte-Carlo-type calculations and against experimental data for elastic electron scattering by the H_2 molecule.

Key words: Electron scattering – T-matrix method – Molecular orientation averaging.

1 Introduction

In earlier papers of this series [1–3], hereafter referred to as Parts I–III, we have developed a special type of Gaussian basis sets for use in elastic and inelastic electron scattering calculations. We call them cubic-grid Gaussian basis sets because they are formed by primitive s-type Gaussians distributed at cubic lattice points within a sphere. So far we have only used them in context of the T-matrix expansion method [4], but there is every reason to believe that it also will be profitable to use them in more sophisticated calculations. In Part I [1] we optimized the cubic-grid basis set for the best representation of the plane-wave and Green functions. The necessary formulas for the matrix elements of the Green function and the interaction potential between the scattering electron and the target molecule were derived in Part II [2]. In Part III [3] we tested the response of the calculated cross section to the choice of the sphere size, i.e., to the size of the cubic-grid basis set, and to translation of the target molecule within the sphere, and we described an approximate correction for contributions from the part of space that lies outside the sphere.

Our next intended step is to apply this approach to molecules. However, for comparison of calculated cross sections with experimental gas-phase data we have to average the calculated cross section over the isotropic orientation of the target molecule with respect to the directions of the incoming and scattered electron. Derivation of a formula for the averaged differential cross section is the subject of this paper. We also report two refinements of the computational scheme described in Parts I–III: (i) we recognize the energy dependence of the constants C_1 and C_2 needed in the evaluation of the matrix elements of the Green function, and (ii) we include the second-order polarization effect by the method of Klonover and Kaldor [5].

2 Theory

Our task is to express an average value of the differential cross section for fixed energies of the incoming and outgoing electrons represented by plane-wave functions $|\boldsymbol{k}^{\mathrm{in}}\rangle$ and $|\boldsymbol{k}^{\mathrm{out}}\rangle$ and a fixed scattering angle ω between $\boldsymbol{k}^{\mathrm{in}}$ and $\boldsymbol{k}^{\mathrm{out}}$

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\omega, k^{\mathrm{out}}, k^{\mathrm{in}}) = \frac{\displaystyle\int \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\omega, k^{\mathrm{out}}, k^{\mathrm{in}}, \Xi)\,\mathrm{d}\Xi}{\displaystyle\int \mathrm{d}\Xi}, \tag{1}$$

where Ξ is a collective symbol for coordinates defining the orientation of a target molecule with respect to the scattering electron. For unnormalized plane-wave functions the differential cross section is given as

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{1}{16\pi^2}\frac{k^{\mathrm{out}}}{k^{\mathrm{in}}}\langle \boldsymbol{k}^{\mathrm{out}}|T\,|\boldsymbol{k}^{\mathrm{in}}\rangle\langle \boldsymbol{k}^{\mathrm{in}}|T\,|\boldsymbol{k}^{\mathrm{out}}\rangle, \tag{2}$$

where k^{in} and k^{out} are absolute values of $\boldsymbol{k}^{\mathrm{in}}$ and $\boldsymbol{k}^{\mathrm{out}}$. Upon expanding the unnormalized plane-wave function in a cubic-grid Gaussian basis set [2]

$$|\boldsymbol{k}\rangle = F(k, k_{\mathrm{g}})\sum_i |s_i\rangle\langle s_i|\boldsymbol{k}\rangle \tag{3}$$

we can rewrite the T-matrix element as

$$\langle \boldsymbol{k}^{\mathrm{out}}|T\,|\boldsymbol{k}^{\mathrm{in}}\rangle = F(k^{\mathrm{out}}, k_{\mathrm{g}})F(k^{\mathrm{in}}, k_{\mathrm{g}})\sum_{i,j}\langle \boldsymbol{k}^{\mathrm{out}}|s_i\rangle\langle s_i|T\,|s_j\rangle\langle s_j|\boldsymbol{k}^{\mathrm{in}}\rangle. \tag{4}$$

To avoid unnecessary repetition of our derivation from Part I [1] we only note that $F(k, k_{\mathrm{g}})$ is a "correction" factor

$$F(k, k_{\mathrm{g}}) = \frac{2^{-3/2}}{D}\exp\left[\frac{3}{4}\left(\frac{k}{k_{\mathrm{g}}}\right)^2\right],$$
$$D = 1 + 4\exp\left(-\frac{\pi^2}{12}\right) + 4\exp\left(-\frac{\pi^2}{6}\right) \tag{5}$$

and s_i are s-type primitive Gaussians with an exponent $\alpha = k_{\mathrm{g}}^2/3$ distributed in a regular cubic lattice within a sphere. The constant k_{g} is also used for the definition of the grid, $\pi/2k_g$. Substitution for the expansion coefficients in Eq. (4)

$$\langle \boldsymbol{k}^{\text{out}}|s_i\rangle = \left(\frac{2\pi}{\alpha}\right)^{3/4} \exp\left(-\frac{(\boldsymbol{k}^{\text{out}})^2}{4\alpha}\right)\exp(-\mathrm{i}\boldsymbol{k}^{\text{out}}\boldsymbol{A}_i) \tag{6}$$

$$\langle s_j|\boldsymbol{k}^{\text{in}}\rangle = \left(\frac{2\pi}{\alpha}\right)^{3/4} \exp\left(-\frac{(\boldsymbol{k}^{\text{in}})^2}{4\alpha}\right)\exp(\mathrm{i}\boldsymbol{k}^{\text{in}}\boldsymbol{A}_j) \tag{7}$$

leads to the following expression for the T-matrix elements:

$$\langle \boldsymbol{k}^{\text{out}}|T\,|\boldsymbol{k}^{\text{in}}\rangle = A_T(k^{\text{out}}, k^{\text{in}})\sum_{i,j} T_{ij}\exp(-\mathrm{i}\boldsymbol{k}^{\text{out}}\boldsymbol{A}_i + \mathrm{i}\boldsymbol{k}^{\text{in}}\boldsymbol{A}_j), \tag{8}$$

$$\langle \boldsymbol{k}^{\text{in}}|T\,|\boldsymbol{k}^{\text{out}}\rangle = A_T(k^{\text{in}}, k^{\text{out}})\sum_{m,n} T^*_{mn}\exp(+\mathrm{i}\boldsymbol{k}^{\text{out}}\boldsymbol{A}_m - \mathrm{i}\boldsymbol{k}^{\text{in}}\boldsymbol{A}_n). \tag{9}$$

Here $\boldsymbol{A}_i$ are position vectors of the cubic-grid Gaussian functions, T_{ij} and T_{mn} are the T-matrix elements in the cubic-grid basis set, and A_T is a constant defined by

$$A_T(\kappa_1, \kappa_2) = F(\kappa_1, k_g)F(\kappa_2, k_g)\left(\frac{2\pi}{\alpha}\right)^{3/2} \exp\left(-\frac{(\kappa_1^2+\kappa_2^2)}{4\alpha}\right) \tag{10}$$

for arbitrary κ_1 and κ_2. Using the expressions (8) and (9) we may rewrite the differential cross section as

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = A_{\text{DCS}}\sum_{i,j,m,n} T_{ij}T^*_{mn}I_{ijmn}, \tag{11}$$

where A_{DCS} is a constant for specified values of the input parameters k^{in}, k^{out}, and k_g

$$A_{\text{DCS}} = \frac{A_T^2(k^{\text{in}}, k^{\text{out}})}{16\pi^2}\frac{k^{\text{out}}}{k^{\text{in}}}. \tag{12}$$

In expression (11) the only quantity that depends on the directions of $\boldsymbol{k}^{\text{in}}$ and $\boldsymbol{k}^{\text{out}}$ is

$$I_{ijmn} = \exp[\mathrm{i}(\boldsymbol{k}^{\text{in}}\boldsymbol{B}_{jn} + \boldsymbol{k}^{\text{out}}\boldsymbol{B}_{mi})] \tag{13}$$

in which $\boldsymbol{B}_{jn} = \boldsymbol{A}_j - \boldsymbol{A}_n$ and $\boldsymbol{B}_{mi} = \boldsymbol{A}_m - \boldsymbol{A}_i$. Averaging of the differential cross section (11) for a statistical ensemble of randomly oriented molecules is equivalent to integration over all possible orientations of $\boldsymbol{k}^{\text{in}}$ and $\boldsymbol{k}^{\text{out}}$ in Eq. (13) under the boundary conditions of fixed k^{in}, k^{out} and the angle ω between $\boldsymbol{k}^{\text{in}}$ and $\boldsymbol{k}^{\text{out}}$. This average value can be expressed analytically as follows:

$$\bar{I}_{ijmn} = \sum_{k_1=0}^{K_1}\sum_{k_2=0}^{K_2}\sum_{k_3=0}^{K_3} A_{k_1k_2k_3}(a_{im})^{2k_1}(b_{ijmn})^{2k_2}(c_{ijmn})^{2k_3}, \tag{14}$$

where

$$A_{k_1k_2k_3} = 2\frac{(-1)^{k_1+k_2+k_3}(k_1+k_2)!(k_1+k_2+k_3+1)!}{(k_1!)^2(k_2!)^2k_3!(2(k_1+k_2+k_3+1))!} \tag{15}$$

and a_{im}, b_{ijmn}, and c_{ijmn} are constants defined by

$$a_{im} = k^{\text{out}}B_{mi}\sin\omega, \tag{16}$$

$$b_{ijmn} = k^{\text{in}}B_{jn}\sin\chi_{jnmi}, \tag{17}$$

$$c_{ijmn} = k^{\text{in}}B_{jn}\cos\chi_{jnmi} + k^{\text{out}}B_{mi}\cos\omega. \tag{18}$$

The quantity χ_{jnmi} in Eqs. (17) and (18) is the angle between the vectors $\boldsymbol{B}_{jn}$ and $\boldsymbol{B}_{mi}$. The summation limits K_1, K_2, and K_3 are defined in the next section. The analytical formula (14) for a general function $f = \exp[\mathrm{i}(\boldsymbol{k}^a\boldsymbol{A} + \boldsymbol{k}^b\boldsymbol{B})]$ is derived in the Appendix for arbitrary vectors $\boldsymbol{A}$, $\boldsymbol{B}$, $\boldsymbol{k}^a$, and $\boldsymbol{k}^b$.

Averaging becomes somewhat more complicated if we include long-range interactions from the part of the space that lies outside the volume that contains the cubic-grid basis set. As derived in Part III [3], the T-matrix element (4) then contains two additional terms

$$\langle \boldsymbol{k}^{\mathrm{out}} | T | \boldsymbol{k}^{\mathrm{in}} \rangle = F_{\mathrm{out}} F_{\mathrm{in}} \sum_{i,j} \langle \boldsymbol{k}^{\mathrm{out}} | s_i \rangle \langle s_i | T - U_s | s_j \rangle \langle s_j | \boldsymbol{k}^{\mathrm{in}} \rangle + \frac{4\pi}{Q^2} \sum_C Z_C^{\mathrm{eff}} \mathrm{e}^{\mathrm{i}\boldsymbol{Q}\boldsymbol{R}_C}, \tag{19}$$

where

$$\boldsymbol{Q} = \boldsymbol{k}^{\mathrm{in}} - \boldsymbol{k}^{\mathrm{out}}. \tag{20}$$

The U_s-matrix elements are given [3] by

$$\langle s_i | U_s | s_j \rangle = 2 \left\langle s_i \left| \sum_C \frac{-Z_C^{\mathrm{eff}}}{|\boldsymbol{r} - \boldsymbol{R}_C|} \right| s_j \right\rangle. \tag{21}$$

The summation index C runs over the atoms of the target molecule and Z_C^{eff} are their effective atomic charges chosen so as to reproduce the long-range electrostatic potential generated by the molecule. On substituting into Eq. (2) from Eq. (19) we obtain

$$\begin{aligned} \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{1}{16\pi^2} \frac{k^{\mathrm{out}}}{k^{\mathrm{in}}} \Biggl\{ & A_T^2 \sum_{i,j,m,n} (T - U_s)_{ij} (T - U_s)^*_{mn} I_{ijmn} \\ & + \frac{4\pi}{Q^2} A_T \sum_{i,j,C} Z_C^{\mathrm{eff}} [(T - U_s)_{ij} + (T - U_s)^*_{ij}] I_{ijcc} \\ & + \frac{16\pi^2}{Q^4} \sum_{C,D} Z_C^{\mathrm{eff}} Z_D^{\mathrm{eff}} I_{CCDD} \Biggr\}. \end{aligned} \tag{22}$$

As in expansion (11), the only quantities that depend on the directions of $\boldsymbol{k}^{\mathrm{in}}$ and $\boldsymbol{k}^{\mathrm{out}}$ are the I terms, and these can be averaged by use of Eq. (14).

3 Expression of Bessel functions by finite power series in the average value formula

Three summations over the indices k_1, k_2, and k_3 in expression (14) originate from an approximation of the Bessel functions by a finite power series, namely of two Bessel functions of the zeroth order in Eq. (A.14) and one Bessel function $J_{k_1+k_2+1/2}$ in Eq. (A.18). We show in this paragraph how to determine the numbers K_1, K_2, and K_3 of terms in the respective power series that have to be taken into account in order to evaluate the integral (14) with an accuracy of 10^{-8}.

Let us start with the function $J_0(x)$. As depicted in Fig. 1, the quality of the power series approximation improves with the increasing value of the summation limit (K_1 or K_2). Thus, the higher are the values of an argument x (which is a_{im} or b_{ijmn} in our case), the higher are the summation limits K_1 and K_2 that have to be used. As is seen in Fig. 2, the dependence of the adequate summation limit K_1 and

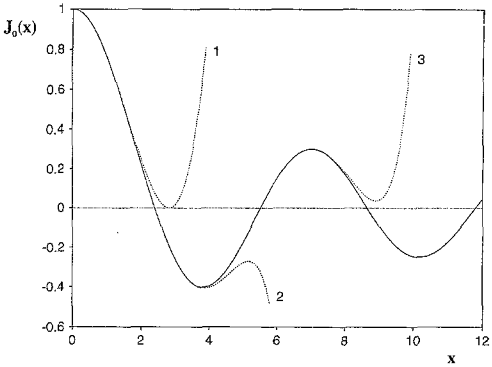

Fig. 1. Approximation of the Bessel function $J_0(x)$ (——) by the finite power series (B.3) (·····) for different values of the summation limit K; (1) $K = 2$, (2) $K = 5$, (3) $K = 10$

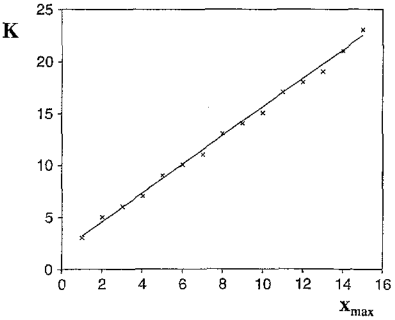

Fig. 2. The summation limit K for an approximation of the Bessel function $J_0(x)$ by the finite power series (B.3) with an accuracy of 0.001 for x ranging from 0 to $x_{\max}$

K_2 on the argument x is linear. This dependence is used in our computer program for the estimation K_1 and K_2 for any set of indices i, j, m, and n.

For the Bessel functions $J_{k_1+k_2+1/2}(x)$, the summation limit K_3 is fixed so as to be applicable also to the Bessel functions $J_{m+1/2}(x)$ with $m = 0, 1, \ldots, K_1 + K_2$, giving a good approximation to all these functions by the truncated power series. The values of K_3 for several half-numbered Bessel functions are summarized in Table 1. The systematic decrease of K_3 with the increasing order of the Bessel function shows that it can always be assigned a value that is sufficient for $J_0(x)$.

We tested the formula (14) against results of Monte-Carlo-type calculations. Let the vectors $\boldsymbol{k}^{\text{in}}$ and $\boldsymbol{k}^{\text{out}}$ be defined by the Euler angles α, β, and γ. Then for a set of fixed parameters A, B, k^a, k^b, ω, and χ (see the Appendix) the statistical average value of the function $f = \exp[\mathrm{i}(\boldsymbol{k}^a\boldsymbol{A} + \boldsymbol{k}^b\boldsymbol{B})]$ may be obtained as

$$\overline{f_{\text{st}}} = \frac{\sum_{i=1}^{N} f(\alpha_i, \beta_i, \gamma_i) p_i}{\sum_{i=1}^{N} p_i}, \tag{23}$$

where the Euler angles α_i, β_i, and γ_i are randomly generated in the ranges $(0, 2\pi)$, $(0, \pi)$, and $(0, 2\pi)$, respectively, and

$$p_i = \sin \beta_i \tag{24}$$

is a statistical weight needed for a uniform coverage of the integration sphere by randomly generated pairs of $\boldsymbol{k}$ vectors. The physical significance of the number of calls of the generator, N, is the number of random orientations of a molecule or, equivalently, the number of randomly oriented molecules. We tested the formula

Table 1. Values of the constants K_1 and K_2 for the Bessel function $J_0(x)$, and K_3 for the Bessel function $J_{m+1/2}(x)$

Parameter and function	Summation limits[a] K_1, K_2, and K_3														
x_{max}	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
$J_0(x)$	3	5	6	7	9	10	11	12	14	15	17	18	19	21	22
$J_{1/2}(x)$	3	4	6	7	8	10	11	12	14	15	16	18	19	20	22
$J_{3/2}(x)$	2	4	5	7	8	9	11	12	13	14	16	17	18	20	21
$J_{5/2}(x)$	2	3	5	6	7	9	10	11	13	14	15	17	18	19	21
$J_{7/2}(x)$	2	3	4	5	7	8	9	11	12	13	15	16	17	19	20
$J_{9/2}(x)$	2	2	3	5	6	7	9	10	11	13	14	15	16	18	19

[a] For the tabulated K_1, K_2, and K_3 values, the Bessel functions are evaluated with an accuracy of 0.001 for x in the range $(0, x_{max})$. Note that K_3 is always smaller than or equal to K_1 and K_2

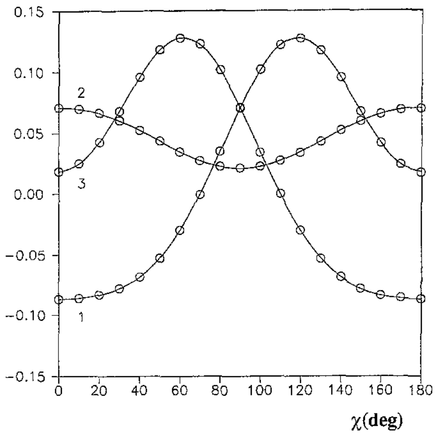

Fig. 3. The angular dependence of the average value of the function f calculated analytically according to Eq. (A.20) (full line) and statistically according to Eq. (23) (open circles) for scattering angles $\omega = 0°(1)$, $\omega = 90°(2)$, and $\omega = 180°(3)$, with the parameters $A = 3$, $B = 5$, $k^a = 0.7$ and $k^b = 1.7$. The number of Monte-Carlo steps was 10^7

(14), expressed as Eq. (A.20), for different values of input parameters and found excellent agreement. An example is shown in Fig. 3.

4 Elastic electron scattering by isotropic H_2

To test our formula for the average value of the differential cross section [Eq. (11)], we performed calculations on elastic scattering of electrons by the H_2 molecule and compared the calculated differential cross sections with experimental data. We selected an electron energy of 10 eV because we anticipate that it will be a typical value in our future calculations, the primary aim of which will be the interpretation of vibrational EELS.

Upon examination of the published data [6–8] it seems to us that the most reliable differential cross sections for elastic electron scattering by H_2 at 10 eV are the data by Srivastava et al. [7], renormalized by Trajmar et al. [8]. In Fig. 4 we plot these data along with the results of our calculations. We tried several cubic-grid basis sets of different sizes and found that the results were converged for the 11 × 11 × 11 basis set. For the H_2 molecule we used either Sadlej's [3*s*1*p*] basis set [9] which was especially developed for SCF calculations of electric properties of molecules and should therefore be suitable for SCF calculations of the interaction

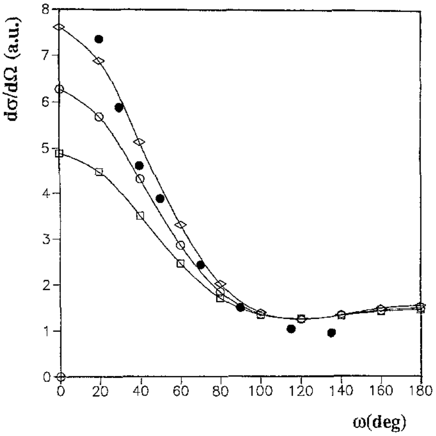

Fig. 4. Differential cross section for elastic scattering of electrons by H_2 (incident energy 10.0 eV). Full circles denote experimental data by Srivastava et al. [7] renormalized by Trajmar et al. [8] and the three curves are results of our calculations: (□) [3*s*1*p*] and 11 × 11 × 11 cubic-grid Gaussian basis set without polarization effect, (○) [3*s*1*p*] and 11 × 11 × 11 cubic-grid Gaussian basis set with polarization effect, (◇) (10*s*5*p*)/[7*s*5*p*] and 13 × 13 × 13 half-spaced. [1–3] cubic-grid Gaussian basis set with polarization effect

potential between the target molecule and a scattering electron or Huzinaga's (10*s*5*p*)/[7*s*5*p*] basis set [10]. The constants C_1 and C_2 for Green function matrix elements were obtained from Eqs. (C.1) and (C.2) in Appendix C, and the polarization effect was included as described in Appendix D. Averaging was done by using Eqs. (11) and (14) and not Eq. (22), because we found that the results were already converged for the 11 × 11 × 11 basis set and it was therefore not necessary to correct for any longer-range contributions.

Our calculations do not agree with experiment as closely as the most sophisticated scattering calculations published up to now (cf. Gibson et al. [11] and references therein). It should be emphasized, however, that our primary aim was to test the formula for averaging and to see whether the dependence of the calculated differential cross section on the scattering angle is qualitatively correct. Calculations of the present type are readily applicable to polyatomic molecules and we hope that they will provide results of the same accuracy as obtained for H_2.

The method requires additional testing, such as an examination of the effect of the basis set used for the target molecule, improved representation of the Green function by using the half-spaced cubic-grid basis set [1], and application to elastic and inelastic electron scattering by other diatomic molecules. Such calculations are in progress.

Appendix

A. Derivation of the average value of the function f

Let $\boldsymbol{A}$ and $\boldsymbol{B}$ be two vectors of constant lengths A and B at a fixed angle χ. These vectors correspond to the "grid" vectors $\boldsymbol{B}_{jn}$ and $\boldsymbol{B}_{mi}$ from Eq. (13) and they are fixed with respect to the molecule. The average value of the function

$$f = \exp[\mathrm{i}(\boldsymbol{k}^a\boldsymbol{A} + \boldsymbol{k}^b\boldsymbol{B})] \tag{A.1}$$

over all possible orientations of the molecule with respect to the fixed pair of vectors $\boldsymbol{k}^a$ and $\boldsymbol{k}^b$ may be evaluated by integration over orientations of the molecule and the pair of the $\boldsymbol{A}$ and $\boldsymbol{B}$ vectors. However, computationally it is preferable to keep the molecule and the vectors $\boldsymbol{A}$ and $\boldsymbol{B}$ fixed and to average over all possible orientations of vectors $\boldsymbol{k}^a$ and $\boldsymbol{k}^b$, keeping their lengths k^a and k^b and their mutual angle ω constant.

We choose a molecule-fixed (unprimed) Cartesian coordinate system such that $\boldsymbol{A} = (0, A_y, A_z)$ and $\boldsymbol{B} = (0, 0, B_z)$. We define a rotating (primed) Cartesian coordinate system in which the Cartesian components of the $\boldsymbol{k}^a$ and $\boldsymbol{k}^b$ vectors are fixed:

$$\begin{aligned} k_1^{a'} &= 0, & k_1^{b'} &= k^b \sin\omega, \\ k_2^{a'} &= 0, & k_2^{b'} &= 0, \\ k_3^{a'} &= k^a, & k_3^{b'} &= k^b \cos\omega. \end{aligned} \tag{A.2}$$

The orientation of the primed system with respect to the unprimed system is described by the Euler angles α, β, and γ. The relation between the coordinates of $\boldsymbol{k}^a$ and $\boldsymbol{k}^b$ in the two coordinate systems is [12, 13]

$$k_i^b = \sum_{j=1}^{3} A_{ji} k_j^{b'}, \tag{A.3}$$

where

$$\boldsymbol{A} = \begin{pmatrix} \cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma & \sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma & -\sin\beta\cos\gamma \\ -\cos\alpha\cos\beta\sin\gamma - \sin\alpha\cos\gamma & -\sin\alpha\cos\beta\sin\gamma + \cos\alpha\cos\gamma & \sin\beta\sin\gamma \\ \cos\alpha\sin\beta & \sin\alpha\sin\beta & \cos\beta \end{pmatrix}. \tag{A.4}$$

We need the average value of f over all possible orientations of the primed coordinate system. The average value $\bar{f}$ is given by

$$\bar{f} = \frac{\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} f(\alpha, \beta, \gamma)\sin\beta \, \mathrm{d}\alpha \, \mathrm{d}\beta \, \mathrm{d}\gamma}{\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} \sin\beta \, \mathrm{d}\alpha \, \mathrm{d}\beta \, \mathrm{d}\gamma}. \tag{A.5}$$

In view of Eqs. (A.3) and (A.4) we may write

$$k_3^b(\beta, \gamma) = -k^b \sin\omega \sin\beta \cos\gamma + k^b \cos\omega \cos\beta. \tag{A.6}$$

The expression (A.5) can be rewritten using Eqs. (A.1) and (A.6) as

$$\bar{f} = \frac{1}{8\pi^2}\int_0^{2\pi} \mathrm{d}\alpha \int_0^{\pi} \mathrm{d}\beta \sin\beta \exp[\mathrm{i}(\boldsymbol{k}^a(\alpha, \beta)\boldsymbol{A} + k^b B \cos\omega \cos\beta)] \, {}^{\gamma}I(\beta). \tag{A.7}$$

The index γ denotes the integration variable in the integral

$${}^{\gamma}I(\beta) = \int_0^{2\pi} \mathrm{d}\gamma \exp(-\mathrm{i}k^b B \sin\omega \sin\beta \cos\gamma). \tag{A.8}$$

This integral equals 2π multiplied by a Bessel function of the zeroth order [cf. Eq. (B.1)]

$${}^{\gamma}I(\beta) = 2\pi J_0(a \sin\beta), \tag{A.9}$$

where $a = k^b B \sin\omega$ is a constant. Then by using expressions (A.7) and (A.9), and relations

$$k_2^a(\alpha, \beta) = k^a \sin\beta \sin\alpha, \tag{A.10a}$$

$$k_3^a(\alpha) = k^a \cos\beta, \tag{A.10b}$$

$$A_2 = A\sin\chi, \tag{A.10c}$$

$$A_3 = A\cos\chi \tag{A.10d}$$

we may express $\bar{f}$ in the form

$$\bar{f} = \frac{1}{4\pi}\int_0^{\pi} \mathrm{d}\beta \sin\beta \exp[\mathrm{i}(k^a A\cos\chi\cos\beta + k^b B\cos\omega\cos\beta)] J_0(a\sin\beta)\,{}^{\alpha}I(\beta), \tag{A.11}$$

where ${}^{\alpha}I(\beta)$ represents the integral

$${}^{\alpha}I(\beta) = \int_0^{2\pi} \mathrm{d}\alpha \exp(\mathrm{i}k^a A\sin\chi\sin\beta\sin\alpha). \tag{A.12}$$

According to Eq. (B.2) this integral leads again to a Bessel function

$${}^{\alpha}I(\beta) = 2\pi J_0(b\sin\beta) \tag{A.13}$$

with a constant $b = k^a A\sin\chi$. If we next define a constant $c = k^a A\cos\chi + k^b B\cos\omega$, we get from Eqs. (A.11) and (A.13)

$$\bar{f} = \frac{1}{2}\int_0^{\pi} \mathrm{d}\beta \sin\beta \exp(\mathrm{i}c\cos\beta) J_0(a\sin\beta) J_0(b\sin\beta). \tag{A.14}$$

The expansion of Bessel functions into the infinite power series (B.3) and neglect of terms with higher exponents permit us to approximate $\bar{f}$ by

$$\bar{f} \approx \frac{1}{2}\sum_{k_1=0}^{K_1}\sum_{k_2=0}^{K_2} P_{k_1} Q_{k_2}\,{}^{\beta}I_{k_1k_2}, \tag{A.15}$$

where the terms P_{k_1} and Q_{k_2} are

$$P_{k_1} = \frac{(-1)^{k_1}}{(k_1!)^2}\left(\frac{a}{2}\right)^{2k_1}, \tag{A.16a}$$

$$Q_{k_2} = \frac{(-1)^{k_2}}{(k_2!)^2}\left(\frac{b}{2}\right)^{2k_2}. \tag{A.16b}$$

The integral in Eq. (A.15) is

$${}^{\beta}I_{k_1k_2} = \int_0^{\pi} \mathrm{d}\beta \exp(\mathrm{i}c\cos\beta)(\sin\beta)^{2v}, \tag{A.17}$$

where $v = k_1 + k_2 + 1/2 \geqslant 1/2$. Since $\Gamma(1/2) = \pi$, the use of Eq. (B.4) leads to

$${}^{\beta}I_{k_1k_2} = \sqrt{\pi}\,\Gamma(k_1 + k_2 + 1) J_{k_1+k_2+1/2}(c)\left(\frac{2}{c}\right)^{k_1+k_2+1/2}. \tag{A.18}$$

Substituting for ${}^{\beta}I_{k_1,k_2}$ in Eq. (A.15) from Eq. (A.18) we obtain

$$\bar{f} = \sqrt{\pi}\sum_{k_1=0}^{K_1}\sum_{k_2=0}^{K_2} \frac{(-1)^{k_1+k_2}\Gamma(k_1 + k_2 + 1) J_{k_1+k_2+1/2}(c)}{(k_1!)^2(k_2!)^2}\,\frac{(a)^{2k_1}(b)^{2k_2}}{(2c)^{k_1+k_2+1/2}}. \tag{A.19}$$

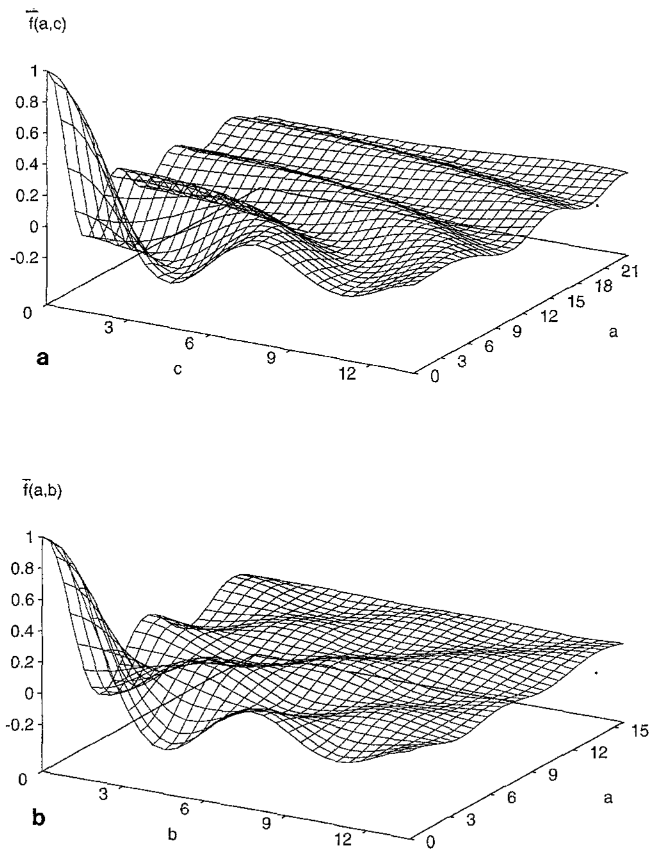

Fig. 5. Two-dimensional plots of the function $\bar{f}(a, b, c)$ for $b = 0$ (**a**) and $c = 0$ (**b**)

Since the integral (B.4) does not depend on the sign of x we may write $|c|$ instead of c in (A.19). This is important because of the condition $|\arg(z)| < \pi$ in the expression (B.5). We may now substitute the series (B.5) for $J_{k_1+k_2+1/2}(c)$, replacing the infinite sum by a finite sum from 0 to K_3. We then express the Gamma functions by means of expressions (B.6) and (B.7) and obtain the final formula

$$\bar{f} \approx \sum_{k_1=0}^{K_1} \sum_{k_2=0}^{K_2} \sum_{k_3=0}^{K_3} A_{k_1k_2k_3}(a)^{2k_1}(b)^{2k_2}(c)^{2k_3}, \tag{A.20}$$

where

$$A_{k_1k_2k_3} = 2\frac{(-1)^{k_1+k_2+k_3}(k_1+k_2)!(k_1+k_2+k_3+1)!}{(k_1!)^2(k_2!)^2k_3!(2(k_1+k_2+k_3+1))!}. \tag{A.21}$$

As expected, $\bar{f}(a, b, c)$ is a dimensionless function, and it equals unity for $a = b = c = 0$. It converges to zero as the parameters a, b, and c go to infinity (Fig. 5).

B. Formulas for the Bessel functions and Gamma function [14, 15]

In all the equations below, v and x are real numbers, z is a complex number and n is a natural number.

$$\int_0^{2\pi} \mathrm{d}\varphi \exp(\mathrm{i}x \cos\varphi) = 2\pi J_0(x) \tag{B.1}$$

$$\int_0^{2\pi} \mathrm{d}\varphi \exp(\mathrm{i}x \sin\varphi) = 2\pi J_0(x) \tag{B.2}$$

$$J_0(z) = \sum_{k=0}^{\infty} \frac{(-1)^k}{(k!)^2}\left(\frac{z}{2}\right)^{2k} \tag{B.3}$$

$$\int_0^{\pi} \mathrm{d}\varphi \exp(\pm\mathrm{i}x \cos\varphi)\sin^{2v}(\varphi) = \sqrt{\pi}\, J_v(x)\Gamma(v+\tfrac{1}{2})\left(\frac{2}{x}\right)^v; \ [\mathrm{Re}(v+\tfrac{1}{2}) > 0] \tag{B.4}$$

$$J_v(z) = \left(\frac{z}{2}\right)^v \sum_{k=0}^{\infty} \frac{(-1)^k}{k!\Gamma(v+k+1)}\left(\frac{z}{2}\right)^{2k}; \quad [|\arg(z)| < \pi] \tag{B.5}$$

$$\Gamma(n+\tfrac{1}{2}) = \frac{(2n)!}{2^{2n}n!}\sqrt{\pi} \tag{B.6}$$

$$\Gamma(n) = (n-1)! \tag{B.7}$$

C. C_1 and C_2 constants for the matrix elements of the Green function

In Part II [2] we derived the matrix elements of the Green function for the cubic-grid Gaussian basis sets. The expression for the real part of the Green function (see Eq. (20) in Part II) contains two adjustable constants C_1 and C_2. We obtained their optimum values by the fitting of the Green function in the Gaussian expansion to the exact Green function. We used an electron energy of 10 eV and used the resulting values of C_1 and C_2 also for other energies. In this paper we present a more refined treatment of C_1 and C_2, in which their dependence on energy is recognized. We optimized C_1 and C_2 for several energies in the range from 2 to 20 eV by least-square fits of the Green function in the Gaussian expansion as described in Part II. The resulting energy dependence of $C_1(E)$ and $C_2(E)$ was then expressed by the following polynomial fits:

$$C_1(E) = \sum_{n=0}^{N_1} a_n E^n, \tag{C.1}$$

$$C_2(E) = \sum_{n=0}^{N_2} b_n E^n, \tag{C.2}$$

where E is the energy of the scattering electron in eV. The optimized parameters a_i and b_i are summarized in Table 2. This table also contains the parameter values for

Table 2. Optimized parameters for the determination of constants $C_1(E)$ and $C_2(E)$ needed for the evaluation of Green function elements in the energy range from 2 to 20 eV

n	Regular basis set		Half-spaced basis set	
	a_n	b_n	a_n	b_n
0	0.344223000D+02	0.308130000D+01	0.604885000D+02	0.143650000D+01
1	−0.621155694D+01	−0.378826789D+00	−0.125149381D+02	−0.119820531D+00
2	0.152869898D+01	0.637297089D−01	0.301944669D+01	0.292256127D−01
3	−0.260458686D+00	−0.672804942D−02	−0.497446820D+00	−0.515043756D−02
4	0.290374359D−01	0.411456664D−03	0.534739810D−01	0.614699819D−03
5	−0.207751391D−02	−0.133358373D−04	−0.368785680D−02	−0.479313470D−04
6	0.916221469D−04	0.176866319D−06	0.156910775D−03	0.231997421D−05
7	−0.226207345D−05		−0.374241819D−05	−0.628929957D−07
8	0.238812159D−07		0.382196336D−07	0.726609004D−09

[a] See Eqs. (C.1) and (C.2), and Sect. 3 in Part II [2]

the evaluation of the constants used in conjunction with the half-spaced cubic-grid basis sets (see Eqs. (23) and (24) in Part II).

D. Second-order polarization effect

We used the procedure of Klonover and Kaldor [5], who included the second-order polarization contribution in a way similar to that used in molecular orbital theory to correct the Hartree–Fock potential for second-order electron correlation effect. Hence the total potential is given as

$$V = V_{\mathrm{SX}} + V^{(2)}, \tag{D.1}$$

where V_{SX} is the static-exchange (Hartree–Fock) potential and $V^{(2)}$ is the second-order term. In the orbital form the Klonover and Kaldor's expression [16] may be rewritten as

$$\langle\alpha|V^{(2)}|\beta|\rangle = \sum_{ijp} \frac{(jp|i\beta)[2(jp|i\alpha) - (ip|j\alpha)]}{\varepsilon + \varepsilon_p - \varepsilon_i - \varepsilon_j} - \sum_{ipq} \frac{(qi|p\alpha)[2(qi|p\beta) - (pi|q\beta)]}{\varepsilon_p + \varepsilon_q - \varepsilon - \varepsilon_i}. \tag{D.2}$$

We follow the original notation [16] so that α and β mean Gaussians from a cubic-grid basis set, p and q are indices of occupied orbitals, i and j are indices of unoccupied orbitals, and $\varepsilon = (k^{\mathrm{in}})^2/2$. For convenience of computer program coding we use the (11/22) notation for the two-electron integrals instead of $\langle 12|12\rangle$.

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