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Towards efficient *ab initio* calculations of electron scattering by polyatomic molecules. I. Efficient numerical quadrature of the UGT term

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Abstract

The UGU term was used as a model of the UGT term and its evaluation by numerical quadrature was examined systematically with a training set of eight molecules. Minimum numbers of points have been determined for radial Gauss-Legendre and angular Lebedev quadratures that preserve the accuracy needed for practical applications. These quadratures are recommended for efficient calculation of electron scattering by polyatomic molecules.

1. Introduction

In many technological applications of plasmas, astrochemistry, DNA research, and some other domains of applied physics and chemistry, the processes initiated by electron impact have been recognized as an important reaction channel. Modeling these processes requires information on elastic and inelastic scattering cross sections of the primary reaction components, intermediates and products. The interest of theoretical physicists has shifted therefore considerably from atoms, diatomics and triatomics to larger molecular targets. However, the existing software does not meet actual needs because the calculations for somewhat more extended systems are technically difficult, unless the rigor of the theory is sacrificed and some approximations are introduced. Also, in contrast to electronic structure calculations, for scattering calculations there is no availability of standard and widely used computational methods and software. A standard evaluation of the UGT and UGU terms in *ab initio* calculations of electron scattering by polyatomic molecules is numerical quadrature (see for example Winstead *et al* 1995, Rescigno *et al* 1995). However, in contrast to electronic structure calculations, there are no universal tools, such as standard basis sets, that could be applied to different target molecules. The problem of numerical quadrature is that the radial points corresponding to high momenta cannot be excluded from the integration. These high-momentum radial points require very high angular quadratures, making the calculations cumbersome. We and the others have solved (Ingr *et al* 2000, Čársky and Čurík 2006) this

problem by a stepwise extension of the size of quadrature, both radial and angular, hoping that the convergence in calculated cross sections will be achieved before the capacity of available computational resources would be exhausted. Success of such an approach depended on the particular molecular target. However, the procedure was time consuming and required considerable human effort. The aim of this paper is to suggest a more practical and well defined procedure that is based on a moderately large quadrature ensuring sufficient accuracy and applicability to large molecules.

2. Computational details

Our search for the optimum numerical quadrature is based on the assumption that the integrand in the UGT term behaves similarly as the integrand in the second-Born terms, and that the optimum numerical quadrature found for the latter may also be used for the former. It is also assumed that for the purpose of examination of the numerical quadrature, it is justifiable to calculate the second-Born terms in the static (st) approximation because it requires larger numerical quadratures than the exchange part of the potential. Hence, the task is to find the optimum quadrature of the principal value of the integral

$$P \int f(x, \Omega) dx d\Omega = \sum_p \sum_i w_p w_i \frac{k_p^2 \langle \mathbf{k}_1 | U_{st} | \mathbf{k}_{pi} \rangle \langle \mathbf{k}_{pi} | U_{st} | \mathbf{k}_2 \rangle - k_0^2 \langle \mathbf{k}_1 | U_{st} | \mathbf{k}_{oi} \rangle \langle \mathbf{k}_{oi} | U_{st} | \mathbf{k}_2 \rangle}{k_0^2 - k_p^2} \times \frac{2k_0}{(1-x_p)^2} \quad (1)$$

for which we have used the substitution

$$x = \frac{k + k_0}{k - k_0} \quad (2)$$

$$k = k_0 \frac{(1+x)}{(1-x)} \quad (3)$$

and

$$dk = \frac{2k_0}{(1-x)^2} dx \quad (4)$$

The calculations were performed for a training set of eight molecules: H₂O, CH₄, CF₄, ethylene, propane, cyclopropane, benzene and uracil. The optimized geometries, molecular orbital and density matrices were obtained by Hartee-Fock calculations with the valence-shell DZP basis set (Dunning and Hay 1977). Static-potential integrals were calculated by means of density fitting as described previously (Čársky 2007 and Čársky 2009). Integrations were performed with the Gauss-Legendre radial and

Lebedev angular quadratures. All calculations were performed for the electron energies of 1, 5, 10 and 20 eV.

3. Quadrature for the radial coordinate

Our first task is to find a suitable quadrature with a minimum number of radial points for the function

$$F(x) = \int f(x, \Omega) d\Omega \quad (5)$$

defined by Eq. (1). For each radial point in the range $-1 \leq x \leq 1$ and the grid of 0.002 we have used the Lebedev angular quadrature with 5810 points (Lebedev and Laikov 1999). This size should guarantee that the integration over angular coordinates is of sufficient accuracy for any radial point. In Fig.1 we present a plot of this function for the benzene molecule.

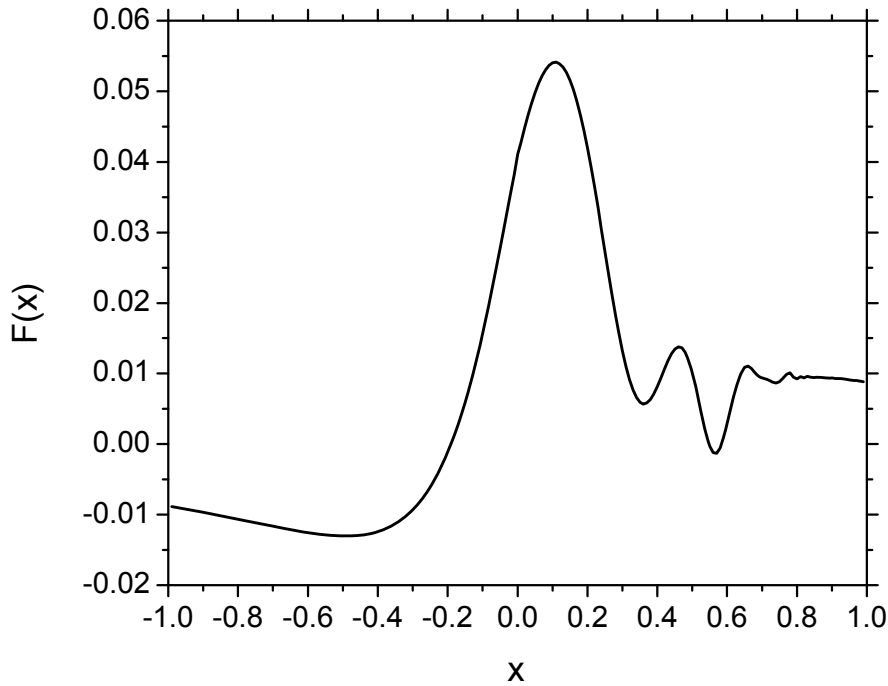


Figure 1. Plot of the function $F(x)$ defined by Eqs. (1) and (5) for the benzene molecule and the electron energy of 10 eV, $\mathbf{k}_1 \parallel x$ and $\mathbf{k}_2 \parallel y$ in the molecular plane xy . The yz plane passes through atoms 1 and 4.

At the first sight it is seen that in the high-energy range of its argument, $F(x)$ is not a function suitable for numerical integration. Also unfavourable is that the higher x is, the higher should be the number of

points in the angular quadrature. However, the uppermost high energy range of x may be disregarded because it holds

$$\lim_{x \rightarrow -\infty} F(x) = \lim_{x \rightarrow \infty} -F(x) \quad (7)$$

which implies that the integration range can be reduced to $-1 + d < x < 1 - d$ without any appreciable loss in accuracy if d is chosen sufficiently small. We adopted such a truncation of the integration ranges by using a new substitution

$$k = k_0 \frac{(a+x)}{(a-x)} \quad (8)$$

$$dk = \frac{2ak_0}{(1-x)^2} dx \quad (9)$$

instead of Eqs. (3) and (4). By setting a larger than 1, the integration range over the radial coordinate is reduced from $(0, \infty)$ to (k_{\min}, k_{\max}) and the minimal and maximum values of k are given as

$$k_{\min} = k_0 \frac{(a-1)}{(a+1)} \quad (10)$$

$$k_{\max} = k_0 \frac{(a+1)}{(a-1)} \quad (11)$$

We assumed nine values for k_{\max} , 100000, 100, 20, 15, 12, 10, 8, 6 and 5 au, and for each integration range (k_{\min}, k_{\max}) we integrated the $F(x)$ function numerically by Simpson method for 1000 radial points. Integration was performed for pairs of \mathbf{k}_1 and \mathbf{k}_2 vectors oriented along the x, y and z axes. The principal values so obtained were squared and averaged for nonequivalent pairs of \mathbf{k}_1 and \mathbf{k}_2 to give quantities resembling differential cross sections (dcs) for scattering angles of 0, 90 and 180°. For H₂O, propane and uracil molecules only scattering angles of 90 and 180° were assumed for testing because for molecules with a nonzero dipole moment the differential cross section for forward scattering is not well defined in the static approximation. The error introduced by setting $a > 1$ was evaluated as $100 \cdot (\text{dcs}(a=1) - \text{dcs}(a > 1)) / \text{dcs}(a=1)$. For a values presented in Table 1 this error was less than 1 % for all three assumed scattering angles and all eight target molecules from the training set.

Table 1 Recommended truncation of the integration range in the Gauss-Legendre radial numerical quadrature and number of radial points (N_{rad})

Molecule	k_0 (eV)	a	k_{min} (au)	k_{max} (au)	N_{rad}
H ₂ O	1	1.07015	0.009	8	24
	5	1.12907	0.037	10	18
	10	1.15388	0.061	12	20
	20	1.22478	0.122	12	18
CH ₄	1	1.07015	0.009	8	10
	5	1.16398	0.046	8	10
	10	1.15388	0.061	12	12
	20	1.17587	0.098	15	10
CF ₄	1	1.07015	0.009	8	26
	5	1.12907	0.037	10	30
	10	1.12124	0.049	15	26
	20	1.17587	0.098	15	22
ethylene	1	1.07015	0.009	8	14
	5	1.12907	0.037	10	14
	10	1.18754	0.073	10	12
	20	1.17587	0.098	15	14
cyclopropane	1	1.09466	0.012	6	14
	5	1.12907	0.037	10	18
	10	1.18754	0.073	10	14
	20	1.22478	0.122	12	12
propane	1	1.09466	0.012	6	14
	5	1.12907	0.037	10	18
	10	1.18754	0.073	10	20
	20	1.27594	0.147	10	18
benzene	1	1.09466	0.012	6	18
	5	1.10641	0.031	12	20
	10	1.24005	0.092	8	18
	20	1.27594	0.147	10	18
uracil	1	1.09466	0.012	6	18
	5	1.12907	0.037	10	38

10	1.18754	0.073	10	38
20	1.27594	0.147	10	18

As expected, the value of k_{\max} increases with the increasing value of k_0 , though the optimum a depends on the particular molecule and with some molecules the increase in k_{\max} is not monotonous. Still, Table 1 can be used for an educated guess for a particular molecule and k_0 if the optimization of a by numerical integration is to be skipped. Fig. 2 and entries of Table 1 show that setting $k_{\max} = 10$ au is a good compromise.

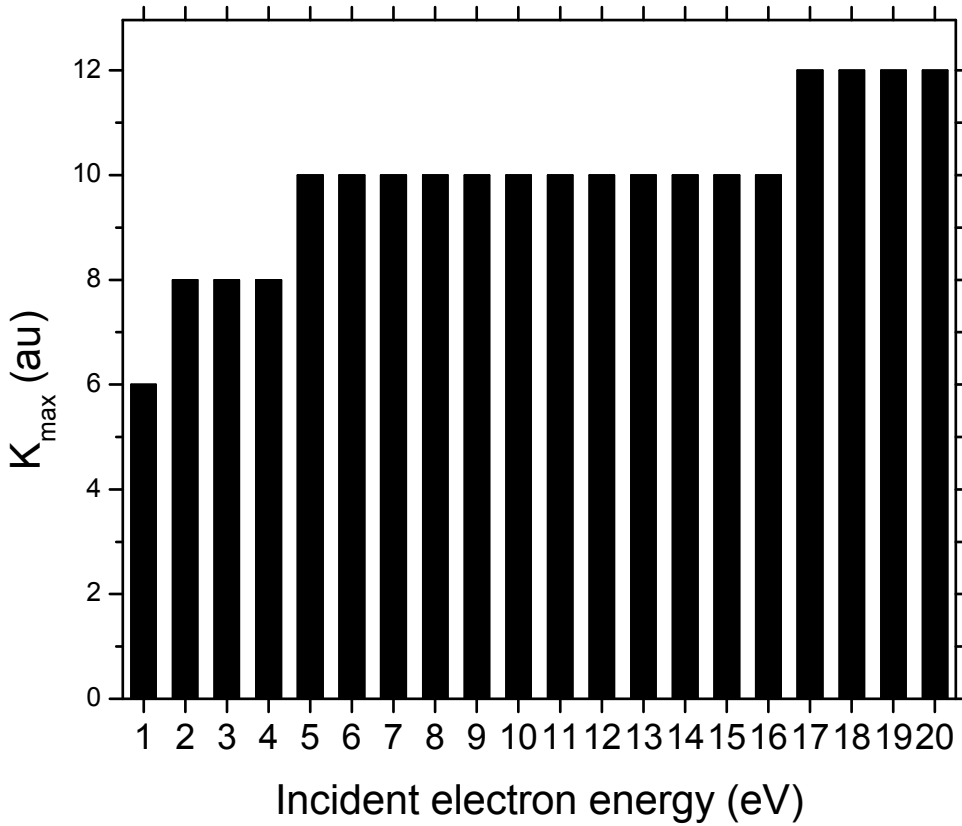


Figure 2. Plot of the recommended k_{\max} for cyclopropane and different energies of the incident electron

The next task was to determine the minimum number of radial points for each integration range (k_{\min} , k_{\max}) that would preserve accuracy of integration to within a preselected threshold. Second-Born principal values P calculated with the number of angular points $N_{\text{ang}} = 5810$ and the number of radial points $N_{\text{rad}} = 80$ were taken as standard. Preserving $N_{\text{ang}} = 5810$ for any radial point, the number of radial points was stepwise increased up to $N_{\text{rad}} = 40$. The principal values so obtained were squared and averaged for nonequivalent pairs of \mathbf{k}_1 and \mathbf{k}_2 to give quantities resembling differential cross sections (dcs) for scattering angles of 0, 90 and 180°. Again, the \mathbf{k}_1 and \mathbf{k}_2 vectors were oriented along x, y, and z

axes. The error introduced by radial quadratures with a particular N_{rad} was evaluated as $100 \cdot (\text{dcs}(N_{\text{rad}} = 80) - \text{dcs}(N_{\text{rad}}) / \text{dcs}(N_{\text{rad}} = 80))$. For H₂O and uracil, the molecules with a high dipole moment, the forward scattering was disregarded for testing. In Table 1 we present minimal radial quadratures so that the defined error was less than 1 % for all pairs \mathbf{k}_1 and \mathbf{k}_2 vectors at the three assumed scattering angles and all eight target molecules from the training set. The size of the radial quadrature depends strongly on the particular molecule. As expected, a higher number of radial points is needed when a high variation of charge density can be expected along the radial coordinate, as it is demonstrated by the pair of molecules CH₄ and CF₄. A high number of radial points for the H₂O molecule can be explained by its high dipole moment. From the entries of Table 1 it can also be concluded that the number of radial points increases with the size of the molecule.

The test calculations indicate that the thresholds of 1% for the determination of a and the number of radial points give results close to the “static-exchange limit”. However, for larger molecules the required number of points in the numerical quadrature may be too high for calculations to be feasible. Hence, for uracil we tested softer thresholds both for the radial and angular quadratures to determine if a less rigorous calculation can maintain its predictive power (see below).

4. Angular quadrature

Having had determined the integration ranges for different electron energies and the minimal numbers of radial points, the next task was to determine the minimal number of angular points for each radial point in the integration ranges ($k_{\text{min}}, k_{\text{max}}$) listed in Table 1. The data obtained with the largest available Lebedev quadrature with $N_{\text{ang}} = 5810$ for all radial points were taken as standard against which the performance of smaller angular quadratures were tested. The principal value in Eq.(1) was squared and averaged for nonequivalent pairs of \mathbf{k}_1 and \mathbf{k}_2 giving the quantities $\text{dcs}_p(N_{\text{ang}} = 5810)$ resembling the differential cross sections for scattering angles of 0, 90 and 180°. For H₂O and uracil scattering angles of only 90 and 180° were assumed. Then for each single radial point p the angular quadrature was performed separately for Lebedev quadratures with 38, 50, 80, 110, 146, 194, 302, and 974 points and with $N_{\text{ang}} = 5810$ for all points other than p . The principal values were squared and averaged as before giving the values $\text{dcs}_p(N_{\text{ang},p})$. For each radial point p we required that the error defined as

$$T_p = 100 \frac{|\text{dcs}_p(N_{\text{ang}} = 5810) - \text{dcs}_p(N_{\text{ang},p})|}{\text{dcs}_p(N_{\text{ang}} = 5810)} \quad (12)$$

be smaller than 1 %. For propane and benzene this requirement was satisfied with the minimum angular quadratures presented graphically in Figures 3 and 4.

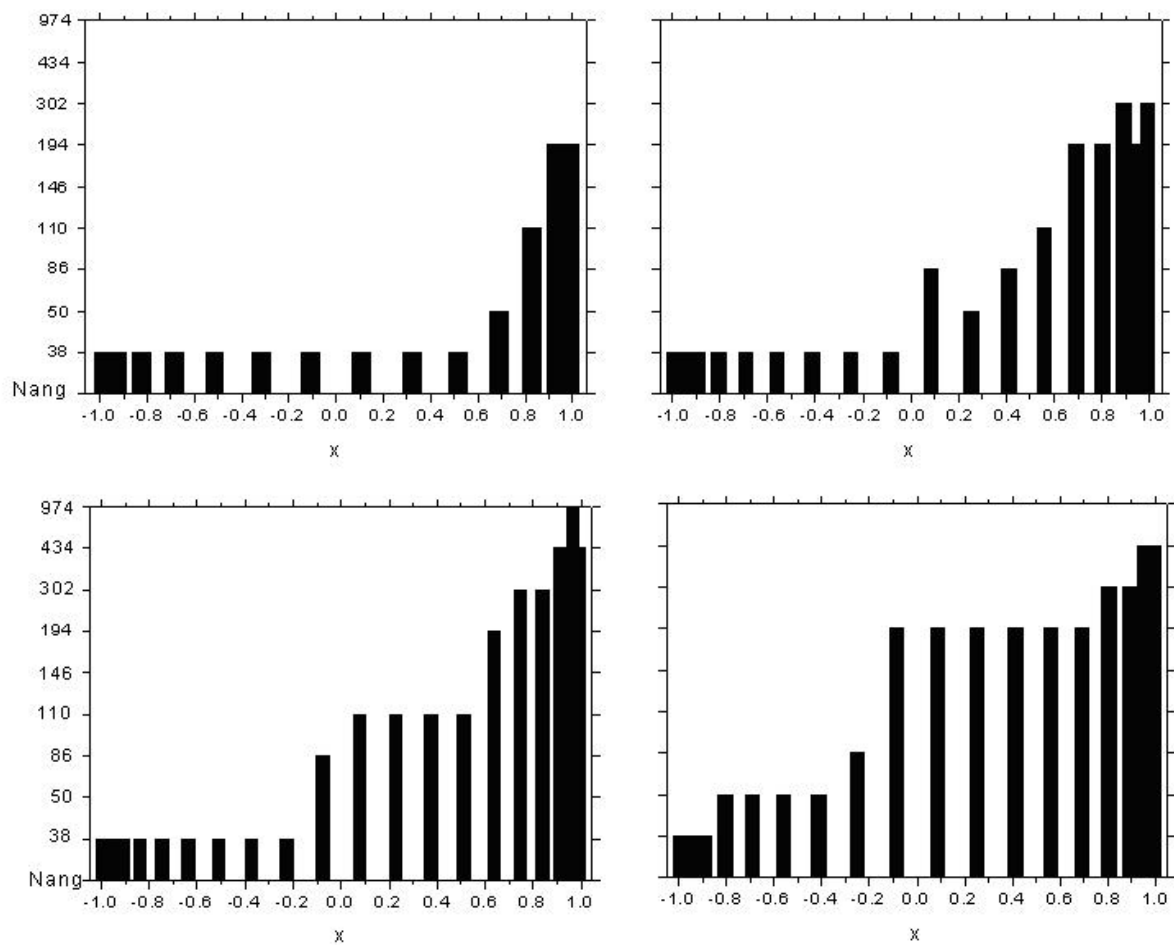


Figure 3. Graphical representation of angular Lebedev quadratures recommended for propane for electron energies of 1 and 5 eV (top) and 10 and 20 eV (bottom). The radial quadratures used are those given in Table 1.

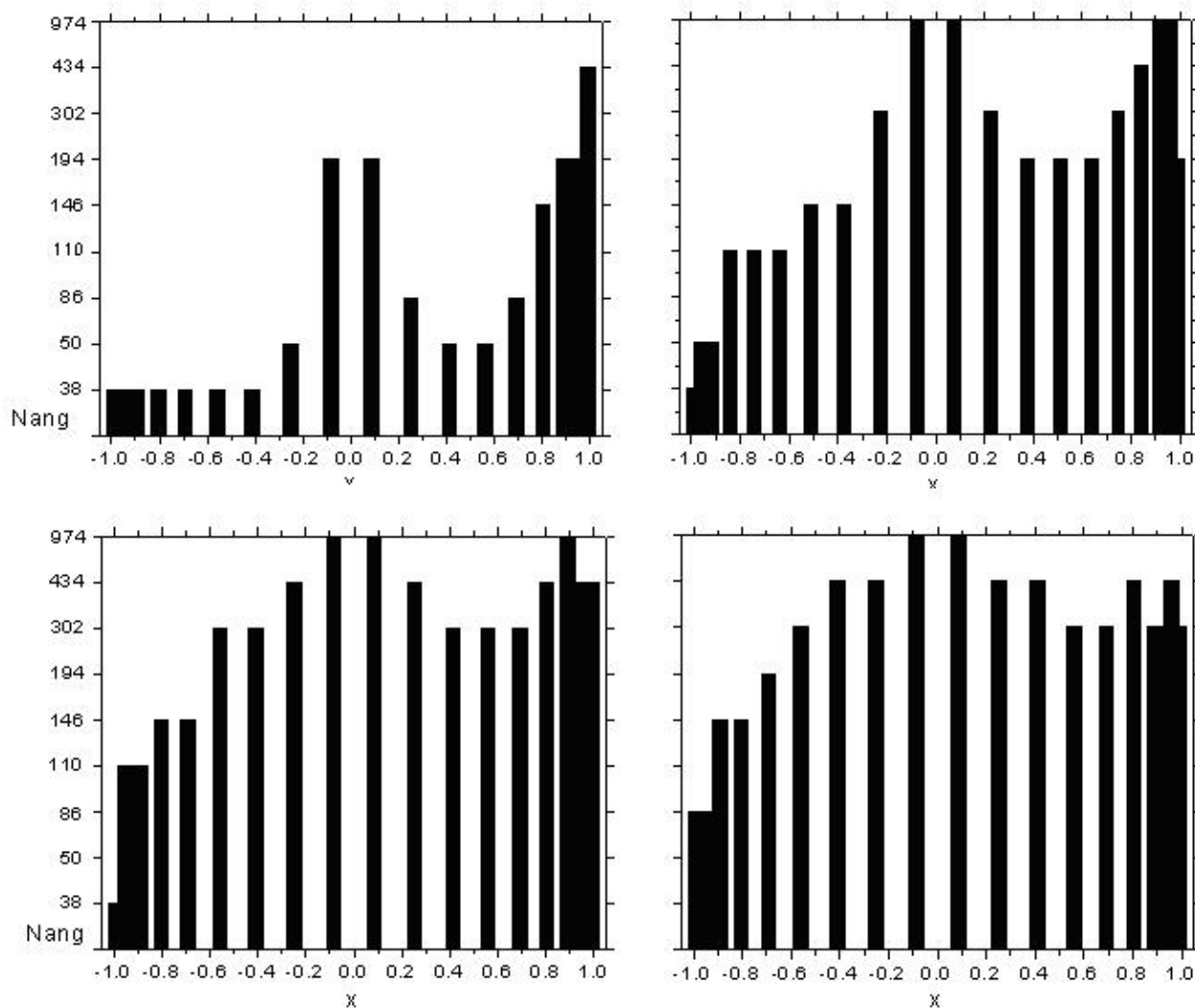


Figure 4. Graphical representation of angular Lebedev quadratures recommended for benzene for electron energies of 1 and 5 eV (top) and 10 and 20 eV (bottom). The radial quadratures used are those given in Table 1.

These plots show some trends that could be expected. A higher number of angular points is required as the radius of the sphere (determined by x and the energy of the incident electron) is increased. With H_2O , CH_4 , CF_4 , and propane the number of angular points increases with x gradually, with ethylene, cyclopropane, benzene and uracil high angular quadratures are also needed for spheres close to k_0 ($x = 0$). Obviously, each molecule requires a special treatment. Still the overall pattern of plots of N_{rad} vs. x for a particular molecule seems to be preserved for the four energies assumed. This allows to guess angular quadratures for different energies. A low number of angular points can be expected with molecules of a near spherical shape, as is the case of the CF_4 molecule. For the electron energy of 10

eV a rather high number of radial points is needed (see Table 1) but the number of angular points needed for 26 radial points is rather low : 12×38 , 50 , 5×86 , 110 , 194 , 302 , 434 , 3×974 , 434 .

For the residue radial point k_0 , $x=0$, a meaningful choice is to use the same number of angular points as for the two neighbouring points with the lowest $|x|$.

For the angular quadratures to be determined as described above, one may expect for total principal values (Eq.(1)) errors smaller than 1% owing to a partial cancellation of errors in individual shells. This indicates that somewhat softer thresholds could be assumed for fixing the number of points for the numerical quadrature. With the uracil molecule we retained the (k_{\min}, k_{\max}) ranges but we relaxed the thresholds to 2, 3 and 4% both for radial and angular quadratures. In Fig.5 we present angular dependences for the three respective angular quadratures. The dashed line represents probably the most accurate calculation reported so far (Winstead and McKoy 2006) for elastic electron scattering by uracil. There is good agreement with our calculation with the largest quadrature. In contrast to our calculation

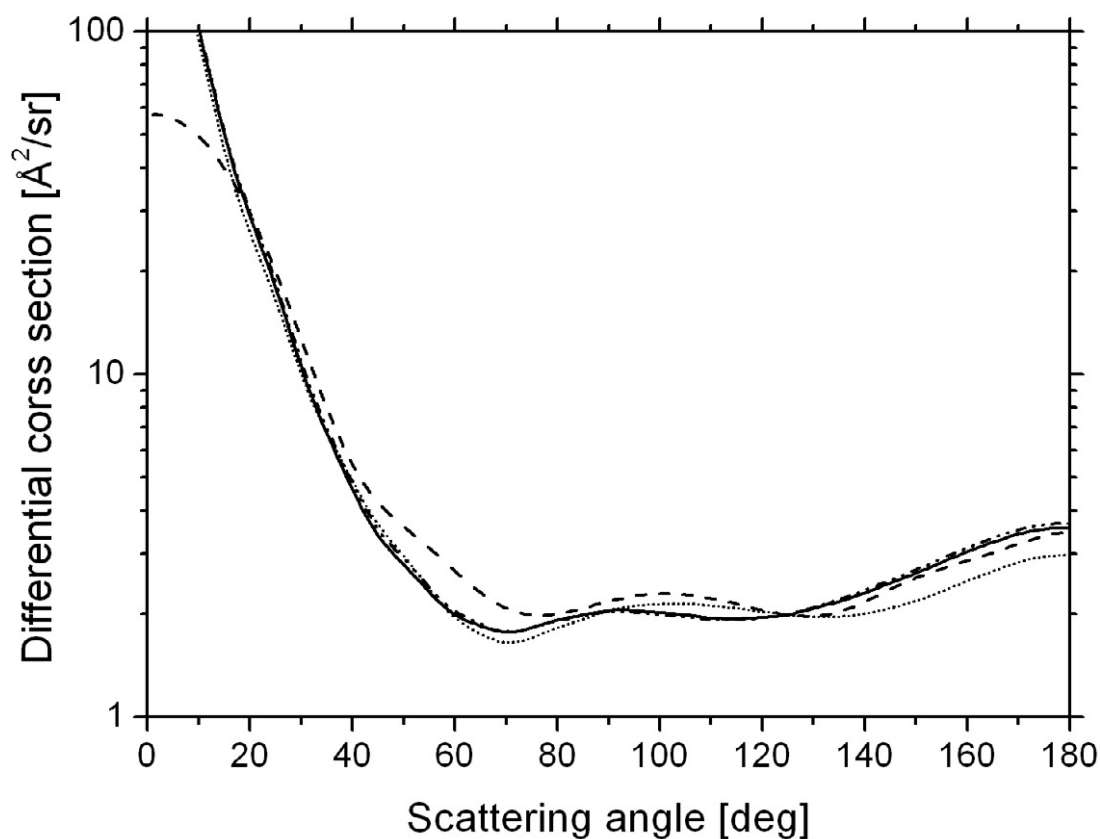


Figure 5. Angular dependence of differential cross section for uracil at the electron energy of 10 eV and the three numerical quadratures with the total numbers of 10 762 points (solid line), 7946 (dashes and dots) and 4202 points (dotted line). The dashed line represents the SEP calculation (Winstead and McKoy 2006).

their calculation includes polarization, which explains the difference in the range of 40 to 80°, where the largest effect of polarization can be expected. Also the shift of the maximum at 100° can be assigned to polarization. The difference at small scattering angles can be explained by a correction for long-range scattering by the dipole (Čársky and Čurík 2006) which was included in our calculation but not in the calculation by Winstead and McKoy (Winstead 2009).

5. Summary

Optimum radial Gauss-Legendre and angular Lebedev quadratures were determined for a training set of 8 molecules. Optimization was done by the following procedure.

1. Use the second-Born term (Eq.(1)) in the static approximation for fixing the optimum quadrature.
2. Reduce stepwise the integration range for the radial coordinate from $(0, \infty)$ to (k_{\min}, k_{\max}) so that the error is less than the preselected threshold.
3. Fix the highest angular quadrature available (5810 points) for each radial point and increase stepwise the radial quadrature until the error in the averaged squares of principal values given by Eq.(1) is less than a preselected threshold (1 % in this paper).
4. For this radial quadrature fix the angular quadrature as described in Section 4.
5. The threshold of 1% for radial and angular quadratures gives results close to the "static-exchange limit". Softer thresholds of 2 or 3% may be more practical, especially for large molecules.

The performance of these fixed quadratures is tested for elastic and vibrationally inelastic scattering in the second paper of this series (Čársky 2010). The second paper also presents a more efficient evaluation of exchange integrals. The third paper of this series (Čurík and Šulc 2010) deals with a more sophisticated inclusion of polarization by means of density functional theory.

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