

Born–Hartree–Bethe approximation in the theory of inelastic electron–molecule scattering

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Abstract

We propose a new approximation in the theory of inelastic electron–atom and electron–molecule scattering. Taking into account the completeness property of atomic and molecular wavefunctions, considered in the Hartree approximation, and using Bethe’s parametrization for electronic excitations during inelastic collisions via the mean excitation energy, we show that the calculation of the inelastic total integral cross-sections (TICS), in the framework of the first Born approximation, involves only the ground-state wavefunction. The final analytical formula obtained for the TICS, i.e. for the sum of elastic and inelastic ones, contains no adjusting parameters. Calculated TICS for electron scattering by light atoms and molecules (He, Ne, and H₂) are in good agreement within the experimental data; results show asymptotic coincidence for heavier ones (Ar, Kr, Xe and N₂).

1. Introduction

Processes of electron–atom and electron–molecule collisions are important in both fundamental [1, 2] and applied [3, 4] science and have been studied for many decades (see, for instance, reviews [5–9] and references therein, also works on electron scattering by rare gas atoms [10–15], by H₂ molecules [16–18], by N₂ molecules [19, 20], and by other diatomic [21, 22] and polyatomic molecules [23–30]).

In this paper we propose a new approximation in the theory of electron–atom and electron–molecule scattering for the calculation of the total integral cross-sections (TICS) for high-energy electron scattering by atoms and molecules in the first Born approximation. The formalism is based on the completeness property of atomic and molecular wavefunctions, considered here in the Hartree approximation, and was recently introduced in work [31], where its efficiency was shown for the TICS for electron scattering by He, Ne and Ar.

Note that the Hartree approximation, being an appropriate one-electron approach to the many-electron wavefunction,

does not take into account the exchange interaction [32], which is generally considered in the Hartree–Fock approximation. However, the quantitative effect of the exchange interaction on electron density (but not on energy) is not too large, at least for light atoms and molecules. For example, the contribution of the exchange interaction to the ground-state electron density of Cu⁺ ion is about several per cent [33] (see figure 1).

In this work we deal with the simplest Hartree description of atomic (or molecular) ground- and excited-state wavefunctions, use Bethe’s parametrization for electronic excitations during inelastic collisions [34] via the mean excitation energy, I , whereas the scattering is considered in the framework of the first Born approximation. So it is natural to name the proposed formalism the Born–Hartree–Bethe approximation.

The main distinctive advantage of the proposed formalism is that the TICS for electron–molecule scattering can be calculated in the presence of minimal available information on the target, namely its ground-state wavefunction and the mean excitation energy; no other parameters or assumptions are needed.

Atomic units are used throughout the work: $e = m = \hbar = 1$.

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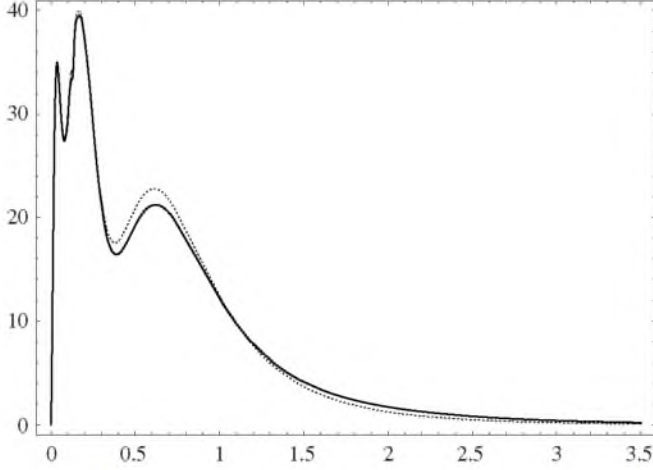


Figure 1. The total radial electron density of the Cu^+ ion according to Pratt [33] for the Hartree (solid line) and the Hartree-Fock (dotted line) approximation.

2. Born-Hartree-Bethe approximation

In the first Born approximation, when electron with initial momentum, \mathbf{p} , scatters on the many-electron target (atom or molecule), the transition probability from the initial state $|i\rangle$ with energy E_i to the final state $|f\rangle$ with energy E_f is determined by (see, for instance, [34])

$$dw_{i \rightarrow f} = 2\pi |\langle f | \mathbf{p}' | U | i \rangle|^2 \delta \left(\frac{p'^2 - p^2}{2} + E_f - E_i \right) \frac{d\mathbf{p}'}{(2\pi)^3}, \quad (1)$$

where

$$U = \sum_{j=1}^A \frac{Z_j}{|\mathbf{r} - \mathbf{R}_j|} - \sum_{j=1}^N \frac{1}{|\mathbf{r} - \mathbf{r}_j|} \quad (2)$$

is the interaction potential of the incident electron and the molecule composed of A nuclei with charges Z_j , coordinates \mathbf{R}_j and N electrons. Further, for short, we will consider only molecules, setting within corresponding calculations $A = 1$ for atoms.

The differential cross-section (DCS) of electron scattering for the transition from the molecular state $|i\rangle$ to state $|f\rangle$ is

$$\frac{d\sigma_{i \rightarrow f}}{d\Omega} = \frac{p'}{4\pi^2 p} \left| \int \langle f | U e^{-i\mathbf{q}\mathbf{r}} | i \rangle d\mathbf{r} \right|^2, \quad (3)$$

where $\mathbf{q} = \mathbf{p} - \mathbf{p}'$ is the electron momentum transfer.

2.1. Elastic scattering

Considering the elastic scattering, when after collision with the incident electron the molecule remains in its initial state, the integral in (3) over the coordinates of the incident electron is computed via the well-known Fourier transform of Coulomb potential,

$$\int e^{-i\mathbf{q}\mathbf{r}'} \frac{d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} = \frac{4\pi}{q^2} e^{-i\mathbf{q}\mathbf{r}}. \quad (4)$$

Then the elastic DCS is

$$\frac{d\sigma_{\text{el}}}{d\Omega} \equiv \frac{d\sigma_{i \rightarrow i}}{d\Omega} = \frac{4}{q^4} \left| \sum_{j=1}^A Z_j e^{-i\mathbf{q}\mathbf{R}_j} - NF(\mathbf{q}) \right|^2, \quad (5)$$

where

$$F(\mathbf{q}) = \frac{1}{N} \langle i | \sum_{j=1}^N e^{-i\mathbf{q}\mathbf{r}_j} | i \rangle \quad (6)$$

is the molecular form factor. The normalizing condition of the molecular ground-state wavefunction $\langle i | i \rangle = 1$ results in $F(0) = 1$.

The obtained elastic DCS depends on the molecular orientation relative to the moving direction of the incident electron. If target molecules are oriented stochastically, the observed elastic TICS is computed by averaging elastic DCS (5) over all possible orientations.

Let us restrict our consideration to the homonuclear diatomic molecules. In this case $N = 2Z$ (note that $N = Z$ for atoms). We choose the reference frame that the point of origin is in the molecular center of mass and the molecular axis $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$ is codirectional to the \mathbf{z} -axis. Then the averaging over all possible molecular orientations is equivalent to the averaging over the direction of \mathbf{q} , i.e. over the solid angle $d\Omega_{\mathbf{q}} = \sin\theta_{\mathbf{q}} d\theta_{\mathbf{q}} d\phi_{\mathbf{q}}$ [35]. Due to axial symmetry the DCS does not depend on $\phi_{\mathbf{q}}$ and the averaging reduces to the integration over the angle between \mathbf{R} and \mathbf{q} :

$$\frac{d\bar{\sigma}_{\text{el}}}{d\Omega} = \frac{1}{2} \int_0^\pi \frac{d\sigma_{\text{el}}}{d\Omega} \sin\theta_{\mathbf{q}} d\theta_{\mathbf{q}}. \quad (7)$$

To calculate the elastic TICS it is preferable to integrate over $dq^2 = 2p^2 \sin\theta d\theta$ instead of $d\Omega$; at that the integration over $d\phi$ reduces to the 2π factor. Evidently, in the case of the elastic scattering q varies from 0 to $q_{\text{max}} = 2p$,

$$\bar{\sigma}_{\text{el}} = \frac{8\pi Z^2}{p^2} \int_0^\pi \sin\theta_{\mathbf{q}} d\theta_{\mathbf{q}} \int_0^{4p^2} |\cos(\mathbf{q}\mathbf{R}/2) - F(\mathbf{q})|^2 \frac{dq^2}{q^4}. \quad (8)$$

2.2. Inelastic scattering and TICS

To calculate the inelastic DCS one must sum the transitional DCS (3) over all final states $|f\rangle$:

$$\frac{d\sigma_r}{d\Omega} = \sum_{f \neq i} \frac{d\sigma_{i \rightarrow f}}{d\Omega}. \quad (9)$$

In the adiabatic approach the molecular wavefunctions depend parametrically on internuclear distance, \mathbf{R} , so from the orthogonality of the initial and final states, $\langle f | i \rangle = 0$, it follows that the electron-nucleus interaction turns into zero:

$$\langle f | \frac{Z}{|\mathbf{r} - \mathbf{R}/2|} + \frac{Z}{|\mathbf{r} + \mathbf{R}/2|} | i \rangle = 0, \quad (10)$$

and the transitional DCS comes to

$$\frac{d\sigma_{i \rightarrow f}}{d\Omega} = \frac{4p'}{q^4 p} \left| \langle f | \sum_{j=1}^N e^{-i\mathbf{q}\mathbf{r}_j} | i \rangle \right|^2. \quad (11)$$

Let us introduce the mean excitation energy of the inelastic electron scattering, I , which determines the mean momentum of scattered electrons, $\bar{p}' = \sqrt{p^2 - 2I}$, and the

mean momentum transfer, $\bar{\mathbf{q}} = \bar{\mathbf{p}}' - \mathbf{p}$. Now in summation over all allowed transitions $|i\rangle \rightarrow |f\rangle$ in (9) one can replace p' and \mathbf{q} , which are specific for the concrete transition, by their mean values and remove them from the sum (9),

$$\frac{d\sigma_r}{d\Omega} = \frac{4\bar{p}'}{q^4 p} \sum_{f \neq i} \left| \langle f | \sum_{j=1}^N e^{-i\mathbf{q}\mathbf{r}_j} | i \rangle \right|^2. \quad (12)$$

To calculate (12) one should use the completeness property of molecular wavefunctions, $\sum_f |f\rangle \langle f| = \hat{\mathbf{I}}$, where $\hat{\mathbf{I}}$ is the unit operator,

$$\begin{aligned} \sum_{f \neq i} \left| \langle f | \sum_{j=1}^N e^{-i\mathbf{q}\mathbf{r}_j} | i \rangle \right|^2 &= \sum_{f \neq i} \sum_{j,k=1}^N \langle i | e^{i\mathbf{q}\mathbf{r}_j} | f \rangle \langle f | e^{-i\mathbf{q}\mathbf{r}_k} | i \rangle \\ &\simeq \sum_{j,k=1}^N [\langle i | e^{i\mathbf{q}(\mathbf{r}_j - \mathbf{r}_k)} | i \rangle - \langle i | e^{i\mathbf{q}\mathbf{r}_j} | i \rangle \langle i | e^{-i\mathbf{q}\mathbf{r}_k} | i \rangle]. \end{aligned} \quad (13)$$

Since in the Hartree approach the many-electron wavefunction of molecule, $|i\rangle = \prod_{j=1}^N \phi_j(\mathbf{r}_j)$, is expressed through the one-electron wavefunctions, $\phi_j(\mathbf{r}_j)$, all terms in double sums over j and k in equation (13) with $j \neq k$ are cancelled, so one easily obtains

$$\sum_{f \neq i} \left| \langle f | \sum_{j=1}^N e^{-i\mathbf{q}\mathbf{r}_j} | i \rangle \right|^2 = N[1 - G(\bar{\mathbf{q}})], \quad (14)$$

where

$$G(\bar{\mathbf{q}}) = \frac{1}{N} \sum_{j=1}^N |\langle \phi_j | e^{-i\bar{\mathbf{q}}\mathbf{r}_j} | \phi_j \rangle|^2, \quad (15)$$

and the inelastic DCS is the following:

$$\frac{d\sigma_r}{d\Omega} = \frac{4N\bar{p}'}{q^4 p} [1 - G(\bar{\mathbf{q}})]. \quad (16)$$

If for each given $\bar{\mathbf{q}}$ the only one-electron shell contributes to $G(\bar{\mathbf{q}})$ then all one-electron matrix elements in the sum in equation (15) are considered to be equal and

$$G(\bar{\mathbf{q}}) \simeq |F(\bar{\mathbf{q}})|^2. \quad (17)$$

Note when $\bar{\mathbf{q}}$ is small from equation (15) it follows

$$G(\bar{\mathbf{q}} \rightarrow \mathbf{0}) \simeq 1 - a\bar{q}^2 + b^2\bar{q}^4, \quad (18)$$

where $a \simeq \langle r \rangle^2$, $b \simeq \langle r^2 \rangle$, so the inelastic DCS (16) diverges when $\bar{q} \rightarrow 0$. $\langle r \rangle$ is the characteristic radius of the atomic shell which mainly contributes to the inelastic TICS at a given incident electron energy.

In the exchange integrals $\int \phi_1(\mathbf{r}_1) \phi_2(\mathbf{r}_2) e^{i\bar{\mathbf{q}}(\mathbf{r}_1 - \mathbf{r}_2)} \phi_1^*(\mathbf{r}_2) \times \phi_2^*(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2$ the parts proportional to $\bar{\mathbf{q}}$ in each exponent's expansion are vanishing due to P-parity of wavefunctions. So exchange integrals are of order of \bar{q}^4 and their contribution to the inelastic DCS is much smaller at small \bar{q} in comparison with direct (non-exchange) integrals. That is another argument for using the Hartree approximation.

The inelastic DCS is also averaged over all molecular orientations in the same manner as in the elastic case,

$$\frac{d\bar{\sigma}_r}{d\Omega} = \frac{1}{2} \int_0^\pi \frac{d\sigma_r}{d\Omega} \sin \theta_q d\theta_q. \quad (19)$$

To calculate the inelastic TICS it is also preferable to integrate over $d\bar{q}^2$, but unlike the elastic scattering the momentum transfer, \bar{q} , cannot be equal to zero: $\bar{q}_{\min} = \bar{p}' - p$. For high-energy electrons the mean excitation energy $I \ll E = p^2/2$ and $\bar{q}_{\min} \simeq I/p$. The upper limit is as for the elastic scattering, $\bar{q}_{\max} = p + \bar{p}' \simeq 2p$, and for the inelastic TICS one obtains,

$$\bar{\sigma}_r = \frac{4\pi Z}{p^2} \int_0^\pi \sin \theta_{\bar{q}} d\theta_{\bar{q}} \int_{(I/p)^2}^{4p^2} [1 - G(\bar{\mathbf{q}})] \frac{d\bar{q}^2}{q^4}. \quad (20)$$

Finally, the TICS for high-energy electron scattering by the homonuclear diatomic molecule is expressed in terms of the ordinary molecular form factor $F(\mathbf{q})$ (6) and the form factor $G(\bar{\mathbf{q}})$ (15) which both are completely determined by the molecular ground-state wavefunction

$$\begin{aligned} \sigma &= \bar{\sigma}_{\text{el}} + \bar{\sigma}_r \equiv \frac{2\pi}{p^2} \left[(2Z)^2 \int_0^\pi \sin \theta_q d\theta_q \right. \\ &\quad \times \int_0^{4p^2} |\cos(\mathbf{q}\mathbf{R}/2) - F(\mathbf{q})|^2 \frac{dq^2}{q^4} \\ &\quad \left. + 2Z \int_0^\pi \sin \theta_{\bar{q}} d\theta_{\bar{q}} \int_{(I/p)^2}^{4p^2} [1 - G(\bar{\mathbf{q}})] \frac{d\bar{q}^2}{q^4} \right]. \end{aligned} \quad (21)$$

We must note, despite the fact that the inelastic DCS can directly be evaluated via equations (16) and (19), its accuracy remains insufficient due to strong dependence on the mean excitation energy I .

3. Computational details

The molecular ground-state wavefunctions, $\phi_j(\mathbf{r})$, were computed *ab initio* [36]. We use the standard basis sets provided by Gaussian98W software package: 6-311++G basis set for H₂ and N₂, 6-311++G(3df,3pd) for He, Ne, Ar and Kr, and 6-31G** for Xe. These basis sets guarantee acceptable accuracy for the calculations of the ground-state wavefunctions. We did not do any examination of the Born–Hartree–Bethe method's accuracy dependence on a basis set size.

Let us provide some useful information on how to compute matrix elements $\langle \phi_j | e^{-i\bar{\mathbf{q}}\mathbf{r}_j} | \phi_j \rangle$, which are needed to calculate the form factors (6) and (15). For example we consider the N₂ molecule.

One-electron wavefunctions of ten internal electrons of N₂, that is five paired molecular orbitals $\phi_j(\mathbf{r})$, are independent of the polar angle φ ,

$$\phi_j(\mathbf{r}) = \phi_j(r, \theta), \quad j = 1, \dots, 5, \quad (22)$$

but one-electron wavefunctions of four valence electrons of N₂, that is two paired molecular orbitals $\phi_{6,7}(\mathbf{r})$, simply depend on polar angle,

$$\phi_{6,7}(\mathbf{r}) = \phi_{6,7}(r, \theta) \{\cos \varphi, \sin \varphi\}. \quad (23)$$

In our reference frame

$$\begin{aligned} \exp(-i\mathbf{q}\mathbf{r}_j) &= \exp(-iqr_j \sin \theta \sin \theta_q \cos \varphi) \\ &\quad \times \exp(-iqr_j \cos \theta \cos \theta_q). \end{aligned} \quad (24)$$

Table 1. The values of the mean excitation energy, I , and estimations for the binding energy of atomic K-electrons, E_K . All values are in eV.

| | H ₂ | N ₂ | He | Ne | Ar | Kr | Xe |
|-------|----------------|----------------|------|-------|-------|-------|-------|
| I | 19.2 | 82.0 | 41.8 | 137.0 | 188.0 | 352.0 | 482.0 |
| E_K | | 611 | | 1280 | 4262 | 17340 | 39235 |

Therefore, the integration over φ in each matrix element $\langle \phi_j | e^{-i\mathbf{q}\mathbf{r}} | \phi_j \rangle$ is analytical and as a result the Bessel functions appear,

$$\begin{aligned} \int_0^{2\pi} e^{-iw \cos \varphi} d\varphi &= 2\pi J_0(w), \\ \int_0^{2\pi} e^{-iw \cos \varphi} \sin^2 \varphi d\varphi &= \frac{2\pi}{w} J_1(w), \\ \int_0^{2\pi} e^{-iw \cos \varphi} \cos^2 \varphi d\varphi &= 2\pi J_0(w) - \frac{2\pi}{w} J_1(w). \end{aligned} \quad (25)$$

Then each matrix element can easily be computed like this one,

$$\begin{aligned} \int \phi_j^2(r, \theta) e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r} &= 2\pi \int \phi_j^2(r, \theta) J_0(qr \sin \theta \sin \theta_q) \\ &\times \cos(qr \cos \theta \cos \theta_q) r^2 \sin \theta d\theta dr. \end{aligned} \quad (26)$$

The imaginary part of the integral is equal to zero due to the symmetry of the one-electron wavefunction.

4. Results and discussion

The values of the mean excitation energy, which are applied for the TICS calculations by equation (21), are shown in table 1 for H₂, N₂, and rare-gas atoms, together with estimations for the binding energy of atomic K-electrons, $E_K = (Z - 0.3)^2/2$, calculated with account for Slater's 1s-shell shielding [37]. For the N₂ molecule we take $Z = 7$ as for N; when considering electron-molecule scattering E_K means a maximal value of those corresponding to atoms in the molecule. I -values are taken from the NIST database [38].

The E_K -values provide an explicit applicability condition of the first Born approximation to electron-atom scattering,

$$E \gg E_K, \quad (27)$$

where $E = p^2/2$ is the incident electron energy.

Results for the TICS for electron scattering by the H₂ molecule are shown in figure 2. They are in good agreement with the experimental data [16–18] (within 10% even for lower energies); when $E > 300$ eV the calculated TICS coincides with the experimental data within the limits of experimental precision. The dotted line shows the contribution of the elastic TICS; it does not exceed 30% of the TICS for the whole energy range. This argues for the importance of correct account for the inelastic TICS contribution, provided by the proposed method. Note that starting from $E = 300$ eV the elastic TICS reaches its minimal constant value, where the condition (27) is apparently satisfied.

In figure 2 in order to demonstrate how the TICS depends on I , the TICS is calculated and presented for values of I which

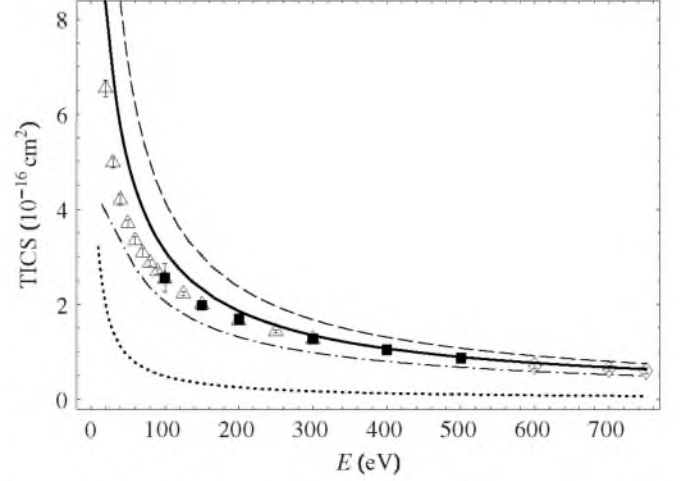


Figure 2. TICS for electron–H₂ scattering as a function of incident electron energy, solid line. Comparison with the experimental data: \triangle [16], \blacksquare [17], \diamond [18]. Elastic TICS, dotted line. The TICS is also presented for values of I which are different from that in table 1: for $I^* = 10$ eV, dashed line, and for $I^* = 38$ eV, dash-dotted line.

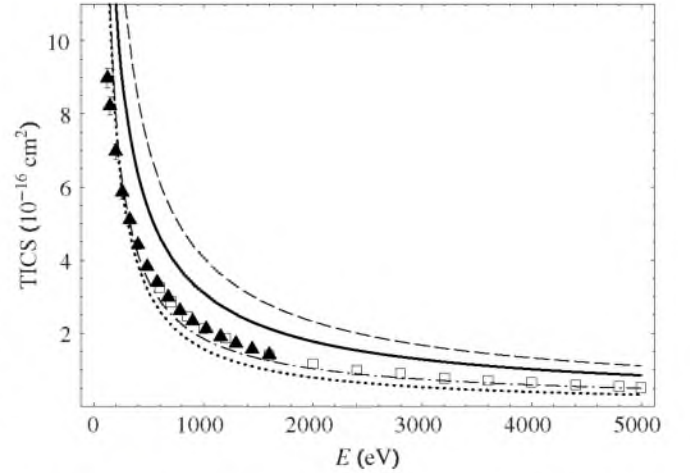


Figure 3. TICS for electron–N₂ scattering as a function of incident electron energy, solid line. Comparison with the experimental data: \blacktriangle [19], \square [20]. Elastic TICS, dotted line. The TICS is also presented for values of I which are different from that in table 1: for $I^* = 41$ eV, dashed line, and for $I^* = 328$ eV, dash-dotted line.

are different from that in table 1 for H₂, namely for its half ($I^* = 10$ eV, dashed line) and double ($I^* = 38$ eV, dash-dotted line) values. Obviously, the dependence is in accordance with equation (20): when I increases the integral over $[1 - G(\mathbf{q})]$ diminishes, and so $\bar{\sigma}_r$ diminishes too.

In figure 3 the results for the TICS for electron scattering by the N₂ molecule are presented. The comparison with the experimental data [19, 20] shows only asymptotic coincidence. Agreement within 50% for energies below 2500 eV and around 30% at 5000 eV confirms that the considered electron energy range does not meet the condition (27). As in the case of H₂ the dotted line shows the contribution of the elastic TICS; it is about 40% of the TICS, but unlike the case of H₂ it does not reach its minimal value even at 5000 eV.

In figure 3 the TICS is calculated and presented for values of I which are different from that in table 1 for N₂, namely for

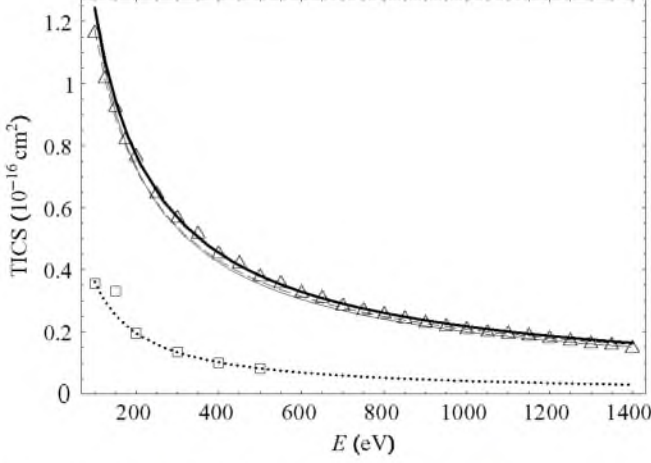


Figure 4. TICS for electron–He scattering as a function of incident electron energy, solid line. Experimental data, Δ [10]; elastic TICS as in equation (28), dotted line, and its comparison with the results of Inokuti and McDowell, \square [14]; calculations of TICS via equation (29), thin solid line; calculations of the inelastic TICS by Inokuti *et al* [15], dashed line.

its half ($I^* = 41$ eV, dashed line) and fourfold ($I^* = 328$ eV, dash-dotted line) values. Note that the TICS for $I^* = 328$ eV coincides much better with experiment; that is due to sizeable decrease of its inelastic part (20).

Calculation of the TICS for electron–atom scattering is more simple because it requires only averaging over $d\Omega$. Keeping in mind that for atomic calculation the number of electrons $N = Z$ (this affects equations (6) and (15)), the TICS for electron–atom scattering is

$$\sigma = \frac{4\pi}{p^2} \left[Z^2 \int_0^{4p^2} |1 - F(\mathbf{q})|^2 \frac{dq^2}{q^4} + Z \int_{(1/p)^2}^{4p^2} [1 - G(\bar{\mathbf{q}})] \frac{d\bar{q}^2}{q^4} \right]. \quad (28)$$

The TICS for electron–He scattering (see figure 4) are in 5%-agreement with the experimental data of Zecca *et al* [10] for $E > 10$ eV. For $E > 100$ eV the coincidence is within the limits of experimental precision. Note that calculation by a simple formula for electron–He scattering (thin solid line in figure 4), derived in [31] assuming $F(\mathbf{q}) = [1 + a^2q^2]^{-2}$, $a = 8/27$,

$$\sigma^{\text{He}} = \frac{4\pi a^2}{3p^2} \left[7Z^2 - 13Z + 24Z \ln \left(\frac{p}{aI} \right) \right], \quad (29)$$

agrees within 5% with our current results.

In figure 4 a comparison of the elastic TICS calculated as in equation (28) with the results of Inokuti and McDowell [14] is presented (dotted line versus \square); the agreement is clear since in both cases the first Born approximation was used. The results of Inokuti *et al* [15] for the inelastic TICS are also shown (dashed line). One can easily see that sum of the Inokuti’s elastic and inelastic TICS overestimates our TICS.

As is shown in figure 5, the results for electron–Ne scattering are in good agreement (within 5%) with the experimental data of Zecca *et al* [11] for $E > 1400$ eV.

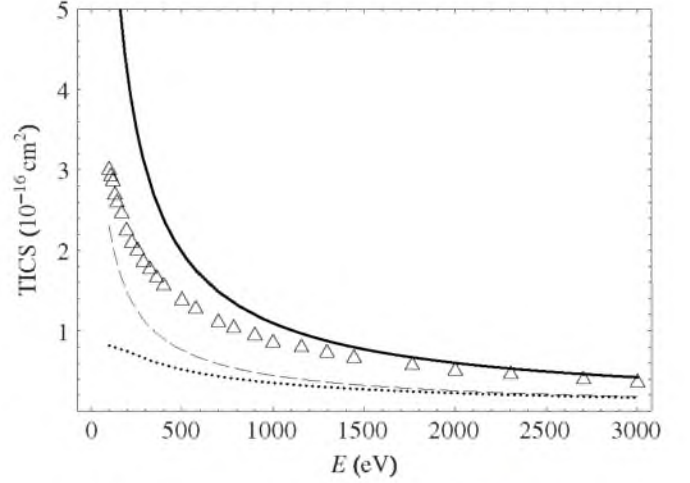


Figure 5. TICS for electron–Ne scattering as a function of incident electron energy, solid line. Experimental data, Δ [11]; inelastic TICS as in equation (28), dotted line, and its comparison with the results of Inokuti *et al* [15], dashed line.

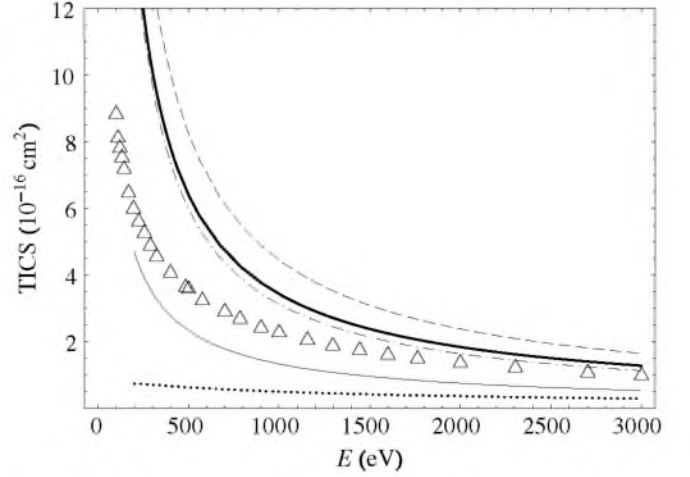


Figure 6. TICS for electron–Ar scattering as a function of incident electron energy, solid line. Experimental data, Δ [11]; inelastic TICS as in equation (28), dotted line, and its comparison with the results of Inokuti *et al* [15], thin solid line. The TICS is also presented for values of I which are different from that in table 1: for $I^* = 47$ eV, dashed line, and for $I^* = 376$ eV, dash-dotted line.

Contribution of the inelastic TICS (dotted line) varies from 20% for low energies to about 40% for $E = 3000$ eV; our results for the inelastic TICS agree well with those of Inokuti *et al* [15] (dashed line) for $E > 1500$ eV, but differ considerably for $E < 1000$ eV.

For electron–Ar scattering (figure 6) the TICS does not coincide with the experimental data of Zecca *et al* [11] even at $E = 3000$ eV. The discrepancy is about 30% for $E < 1500$ eV and 20% for higher energy. The reason for such a disagreement lies in the violation of condition (27).

In figure 6 the TICS is calculated and presented for values of I which are different from that in table 1 for Ar, namely for its quarter ($I^* = 47$ eV, dashed line) and double ($I^* = 376$ eV, dash-dotted line) values. The inelastic TICS is

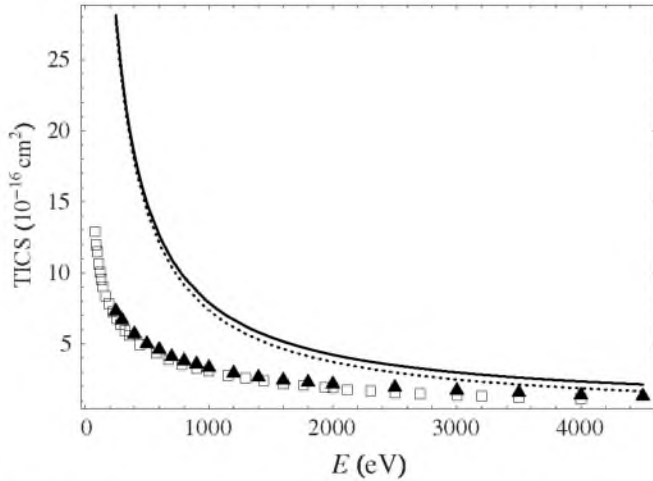


Figure 7. TICS for electron–Kr scattering as a function of incident electron energy, solid line; elastic TICS, dotted line. Comparison with the experimental data: ▲ [12], □ [13].

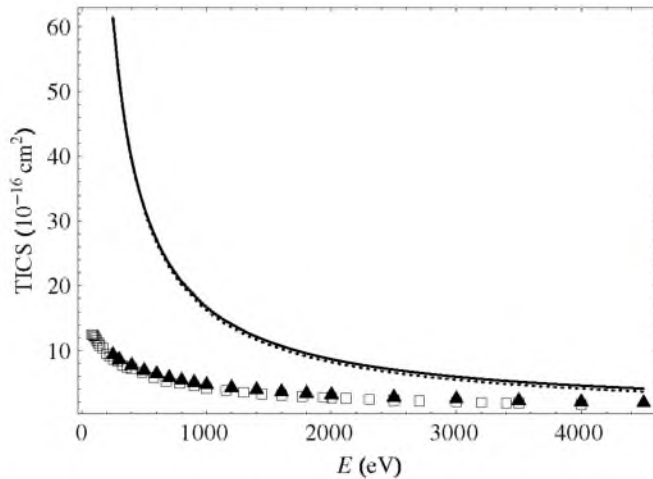


Figure 8. TICS for electron–Xe scattering as a function of incident electron energy, solid line; elastic TICS, dotted line. Comparison with the experimental data: ▲ [12], □ [13].

compared with the results of Inokuti *et al* [15] (dotted versus thin solid line), which exceed our results almost twice.

Calculated TICS for electron scattering by Kr and Xe, presented in figures 7 and 8, differ significantly from corresponding experimental data [12, 13]; the discrepancy is more than 100% for the whole energy range. As in the case of electron–Ar scattering, such a discrepancy is caused by failure of the Born approximation to account for electron scattering when energy of incident electrons is smaller than the atomic E_K .

One can see from figures 7 and 8 the contributions of the elastic TICS (dotted lines) are around 70% for Kr and 90% for Xe, i.e. the excessive value of the elastic part makes the TICS overestimated.

Now let us discuss the applicability of the proposed method. As the method is based upon three independent approximations (Born, Hartree and Bethe), its applicability is in close connection with the related limiting factors. For the first Born approximation it is the condition (27), restricting

the minimal energy of the incident electron beyond which the calculation of TICS becomes quite precise. As indicated above (see figures 4–8 and the related discussion) the discrepancy between the calculated TICS and corresponding experimental values increases along with the atomic Z -number (i.e. along with E_K). Similar behavior is noticed for molecular TICS (figures 2, 3). This argues that the main restriction of the method’s applicability is imposed by the Born approximation. It also concerns the applicability of the method to heavier atoms (or molecules containing them), for which the restriction becomes more severe due to the larger Z .

Concerning the use of the one-electron Hartree approach for wavefunctions instead of the Hartree–Fock or more accurate ones, we can point out the only reason: this allows one to reduce the infinite sum in the equation for inelastic DCS (12), to its simplest form presented in equation (16). Since in the calculation of TICS the ground-state wavefunction is involved, the maximum detriment of using the less precise Hartree approach relates only to the accuracy of the wavefunction and it is quite small (see figure 1).

In the framework of the Bethe approximation one introduces the mean excitation energy, I , as a certain averaged value of electronic excitations during inelastic collision. Dependence of the TICS on I is known almost exactly for He; one may state that in general case at least the asymptotic dependence of the TICS on I has the form like in equation (29). So for large incident electron energy E the TICS logarithmically depends on I -values, i.e. as $\ln(\sqrt{E}/I)$, and the influence of the mean excitation energy on the asymptotic value of the TICS is insignificant. However, as presented in figures 2, 3 and 6, for intermediate energies I has a considerable effect on the TICS.

It is also necessary to point out the distinction between the proposed Born–Hartree–Bethe approximation and the formalism of independent atom treatment (see, for instance, work [21]) for the calculation of the TICS for electron–molecule scattering. For high-energy electrons (~ 10 keV) the molecular target naturally acts as a simple combination of atomic ones, so the molecular TICS becomes a sum of the atomic TICS. The advantage of our method is evinced for intermediate energies (~ 500 – 1000 eV) when the independent atom treatment can fail.

5. Conclusions

In conclusion, we developed a new method for the calculation of inelastic TICS, which is based upon the Born–Hartree–Bethe approximation in the theory of electron–molecule scattering. The main distinction of the method is that the TICS calculation requires only ground-state wavefunction and the mean excitation energy of the target. The method is free of any adjusting parameter and is asymptotically accurate.

For large incident electron energy the TICS is almost independent on the mean excitation energy, since I enters the asymptotic TICS through $\ln(\sqrt{E}/I)$, but for intermediate energies I shows sizeable influence.

The applicability of the method is basically restricted by the Born approximation; if the incident electron energy does not exceed a certain threshold value (binding energy of atomic K-electrons) the results have poor precision. The comparison of the results for electron scattering by H₂, N₂ and rare-gas atoms shows that the discrepancy between the calculated TICS and the corresponding experimental values increases along with Z. The restriction on the method's applicability to heavier atoms (or molecules containing them) becomes more severe due to the larger Z.

Calculated TICS for electron scattering by light atoms and molecules shows a good agreement within the experimental data; perfect coincidence occurs for He for $E > 100$ eV, Ne for $E > 1400$ eV and H₂ for $E > 300$ eV. Results show only asymptotic coincidence for heavier ones (Ar, Kr, Xe and N₂); the reason for this lies in the failure of the first Born approximation to be effective for the TICS calculation in the considered energy ranges.

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