Multiple scattering and electron-uracil collisions at low energies

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Links between two well known methods: methods of zero-range and non-overlapped (muffin-tin) potentials are discussed. Some difficulties of the method of zero-range potentials and its possible elimination are discussed. We argue that such advanced method of ZRP potential can be applied to realistic electron-molecular processes. The method reduces electron-molecule scattering to generalized eigenvalue problem for hermitian matrices and admit fast numerical scheme. A noteworthy feature of the method is direct possibility to calculate the wave functions (partial waves). The theory is applied to electron-uracil scattering. Partial phases and cross-sections at low energies are evaluated and plotted.

Key words: electron-molecule scattering, uracil, multiple scattering, zero-range potential

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I. INTRODUCTION

A growing interest to electron - big molecules (particularly - DNA and RNA bases) scattering leads to a development of one-center expansion of molecular potential methods [1, 2]. However, such expansion seems to become non-effective while molecular dimension grows: a molecular potential may have many local minima which at the one-center expansion leads to extremely non-smooth one-center radial matrix potential. Such difficulty does not appear within the method of non-overlapped potentials (NP).

The notion of the non-overlapped potentials (named as the muffin-tin ones) appears in a context of solid state theory [3] and, further, in scattering theory; it exploits the idea of division of a molecule area into regions - atomic spheres, which surround each atom, such that originally these spheres touch but do not overlap. Inside each of the atomic spheres we replace exact potential by a spherical averaged. Outside the spheres, we can replace the potential by a constant potential (ordinary taken for convenience to be zero). This concept is useful in treatment of both polyatomic molecules and solids. For molecules, this approximation gives a model for calculating electronic energy levels [4] and scattering phases [5]. For crystals the application of the Bloch conditions instead of the boundary condition of scattering theory leads directly to the Korringa-Kohn-Rostoker formalism [6].

There is a special case of the non-overlapped potentials in which radius of the atomic spheres is zero - zero-range potentials (ZRP). The method of ZRP was proposed in 1936 by E. Fermi [7] and has wide applications in photodetachment [8], inelastic scattering [9], and other problem of the quantum physics [10]. In such applications a potential is represented by a boundary condition on a wave function and acts to s-states. There are also generalizations to higher orbital angular momentum states [11, 12]. To our knowledge none of these generalizations have not applied to real molecular processes. It is interesting to characterize some of the sources of the method disability: (i) in realistic situation a choice of the potentials parameters is very
complicated (ii) eigenfunctions for ZRP are singular and sometimes it is not clear how to avoid ambiguity in the treatment of this singularity (iii) it is not clear how to improve results of computations when necessary. In this paper we show that ZRP method (without adjusted parameters), which include some positive features of NP, can cope with realistic processes.

In the section II we show links between zero-range and non-overlapped potentials and discuss how to avoid the problems. We argue that the parameters in generalized boundary condition at an atom can be obtained by solving one-dimension Schrödinger equation. If parameters is known, then partial phases and cross-sections is readily obtained via matrix eigenvalue problem [12].

In the section III we consider an application - low energy electron-uracil (U) scattering. We explain how to extract ZRP parameters from the information provided by a quantum chemistry package. We also summarize the computational steps involved in our calculation and present results of our calculations: partial phases, total and partial cross-sections.

We conclude with a short summary and perspectives.

II. THEORY

As it was mentioned in Introduction, we will consider a polyatomic molecule as a system of spherically symmetric NPs, which we denote as $V_i(|\mathbf{r} - \mathbf{a}_i|)$. It is convenient to write the partial wave $\Psi(\mathbf{r})$ as the linear combination

$$\Psi(\mathbf{r}) = \sum_{i=1}^{N} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} x_{ilm} \Phi_{ilm}(\mathbf{r} - \mathbf{a}_i)$$

of the atomic waves $\Phi_{ilm}(\mathbf{r})$

$$\Phi_{ilm}(\mathbf{r}) = i^l \psi_{ilm}(r) Y_{lm}(\hat{\mathbf{r}}),$$

where $i, l, m$ – atom number and angular momentum quantum numbers correspondingly; $\psi_{ilm} –$ real functions of the radial variable $r$; $Y_{lm}(\hat{\mathbf{r}}) –$ spherical harmonics [14]; $\mathbf{a}_i –$ the vector that marks the point of expansion for each atom; $k –$ radial wave number; $N –$ number of atoms in the molecule. The coefficient $x_{ilm}$ controls the contribution of the wave $\Phi_{ilm}$ to the partial wave. We suppose that outside the potential $V_i(|\mathbf{r} - \mathbf{a}_i|)$ the basis functions $\{\Phi_{ilm}(\mathbf{r})\}$ satisfy the Helmholtz equation [15]. Then outside the NP action the function $\psi_{ilm}$ must be the linear combination $c_2 h_{l+2}^{(2)}(kr) - c_1 h_{l+1}^{(1)}(kr)$ of the outgoing and ingoing spherical Bessel functions [16]. For a partial wave, the coefficients $c_{1,2}$ differ in the phase factor $\exp(2i\delta)$, where $\delta$ is a phase shift. The mentioned choice reflects the condition of equality of the fluxes of the ingoing and outgoing waves at infinity. Without loss of generality we may assume that the function $\psi_{ilm}$ is normalized, so that at infinity

$$\psi_{ilm}(r) = \cos \delta j_l(kr) - \sin \delta y_l(kr),$$

where (we used property 10.1.1 of Ref. [16]) $j_l(x)$ and $y_l(x)$ are regular and singular spherical Bessel functions. To derive differential equation for the functions $\psi_{ilm}(r)$ we expand the partial wave at the vicinity of the point $\mathbf{a}_i$ in the form

$$\Psi(\mathbf{r}_i) = \sum_{lm} x_{ilm} i^l (\psi_{ilm}(r) + w_{ilm} j_l(kr)) Y_{lm}(\hat{\mathbf{r}}),$$

where $\mathbf{r}_i = \mathbf{r} + \mathbf{a}_i$, and substitute the result to Schrödinger equation. The result can be written as inhomogeneous Schrödinger equation for the function $\psi_{ilm}$

$$\left(H - \frac{1}{2} k^2\right) \psi_{ilm}(r) = -w_{ilm} V_i(r) j_l(kr),$$

(3)
where the coefficients $w_{ilm}$ describe the contribution from waves that come from the other NPs, and hamiltonian $H$ is given by the equation

$$
H = -\frac{1}{2} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right) + V_i(r).
$$

Using the properties of the Helmholtz equation solutions [14] one can show that the coefficients $w_{ilm}$ satisfy the equation

$$
w_{ilm} x_{ilm} = \sum_{j(i\neq j)} \sum_{l_1m_1 l_2m_2} x_{jl_1m_1 l_2m_2} l_2^2 Y_{l_2m_2} (\hat{a}_{ij})
\times Q_{l_2m_2l}^{l_1m_1} \left( \cos \delta j_{l_2} (k|a_{ij}|) - \sin \delta y_{l_2} (k|a_{ij}|) \right),
$$

where we denote $a_{ij} = a_i - a_j$; symbol $Q_{l_2m_2l}^{l_1m_1}$ denotes the integral of three spherical harmonics, multiplied by $4\pi$. The upper indices mean that the spherical function with indices $l_1, m_1$ should be complex conjugate. This integral can be expressed in terms of Klebsh-Gordon symbols, or, alternatively, via the $3jm$ Wigner symbols [14]. In particular, by the Wigner-Eckart theorem the integral is proportional to Clebsh-Gordan coefficients [15]:

$$
Q_{l_2m_2l}^{l_1m_1} = \sqrt{4\pi \frac{(2l_2+1)(2l_1+1)}{(2l_1+1)}} C_{l_10}^{l_20} C_{l_1m_1}^{l_1m_1}.
$$

We can see that these symbols are real. From the coefficients properties [14] it follows, that the nonzero symbols correspond to the selection rule $m_1 = m + m_2$, therefore the sum over $m_2$ may be performed explicitly. While account the big $l$ values one can use the selection rule: $l + l_1 + l_2$ - even.

Note that, the function $\psi_{ilm}(r)$ does not coincide with the radial component of the partial wave for $V_i(r)$, because of the nonzero right-hand side of the equation (3). This means that, in general, molecular partial

FIG. 1: Electrostatic potential for ground state of uracil as function of $x, y$. Potential was computed in ab initio calculation and plotted in Hartree units.
FIG. 2: The scattering phases $\delta_{il}(E)$ for different atoms and angular momenta $l = 0, 1$ as functions of incident electron energy. Solid lines: carbon; dashed lines: oxygen; bold lines: nitrogen; dash-dotted lines: hydrogen.

shifts $\delta$ does not coincide with partial shifts $\delta_{il}$ for a NP. However, partial phases $\delta_{il}$, coefficients $w_{ilm}$, and molecular partial shifts $\delta$ are linked by the equality

$$w_{ilm} = \sin \delta (\cot \delta_{il} - \cot \delta).$$

Combining this expression with (4) we see, that the unknown $x_{ilm}$ satisfy the system of linear algebraic equations, which coincide with result of work [12]. In actual calculations values of $l$ are always restricted. If the maximum quantum number for all atoms are the same and equal to $L$, we have the system of $N(L + 1)^2$ equations, which gives the same number of partial waves.

In practice it is convenient to work with matrices and column vectors. Denote the column vector composed of the coefficients $x_{ilm}$ as $|x\rangle$. Next define the matrix $S$, so that

$$S_{ilm,jl_2m_2} = \sum_{l_1=|l_1-l|}^{l_1+l} i^{l_2} Q_{l_2m_2l_1m_1}^l (k|a_{ij}|) Y_{l_2m_2}(\hat{a}_{ij}),$$

(5)

for the case when $i$ and $j$ are different, and in the case $i = j$ nonzero elements are given by $N_{ilm,ilm} = \cot \delta_{il}$. The numbers $ilm$ and $jl_1m_1$ play the role of the multi-indices. It is seen from the last expressions that, the matrix $S$ is positive definite and symmetric with respect to transposition of $jl_1m_1$ and $ilm$, made simultaneously with the operation of complex conjugation (hermicity). The matrix $N$ is also hermitian. The system for the unknown $x_{ilm}$ in the matrix form looks as the eigenvalue problem

$$N|x\rangle = \lambda S|x\rangle$$

(7)

for the eigenvalues $\lambda = \cot \delta$, which are real.

A result of the eigenvalue problem (7) solution is a set of vectors $|x\rangle$ and the partial phases $\delta$. If the molecule has a symmetry, it is possible to classify the phases by irreducible representations of the symmetry...
TABLE I: In the second column corresponding atomic radii \((d_i)\) are presented. In the third and fourth columns \(x_i, y_i\) are coordinates of the position vectors \(a_i\). We also assume \(z_i = 0\).

| Atom | \(d_i\) | \(x_i\)   | \(y_i\)   |
|------|--------|----------|----------|
| C1   | 1.37   | -2.29558 | 0.66988  |
| N2   | 1.23   | -2.14780 | -1.91792 |
| C3   | 1.37   | 0.11224  | -3.21127 |
| C4   | 1.37   | 2.32379  | -2.01273 |
| C5   | 1.37   | 2.37055  | 0.73276  |
| N6   | 1.23   | 0.00000  | 1.86414  |
| H7   | 0.64   | -0.03767 | -5.22343 |
| H8   | 0.64   | 4.08399  | -2.98680 |
| H9   | 0.64   | -3.78218 | -2.82664 |
| H10  | 0.64   | -0.04204 | 3.74037  |
| O11  | 0.93   | -4.30756 | 1.79697  |
| O12  | 0.93   | 4.27587  | 2.02817  |

The multiplicity of degeneration coincide with the dimension of the irreducible subspace. Note, that partial phases, assumed as functions of energy, only of different symmetry can intersect, while the intersection of the partial phases of like symmetry is impossible.

Using known vectors \(|x\rangle\) we can calculate the partial harmonics

\[
A(n) = \sum_{ilm} x_{ilm} \exp(-ikna_i)Y_{lm}(n).
\]

Partial harmonics of the molecular partial waves play the role of spherical harmonics for the spherically symmetric potentials. In analogy with the spherical harmonics, partial harmonics are normalized with respect to integration over angles to the unit. This means that vector \(|x\rangle\) must be normalized, so that \(\langle x|S|x\rangle = 1\). The partial harmonics also may be applied to calculation of the expectation value of angular momentum operator or angular distribution of scattering for any partial wave. For example, partial differential cross section has the form [17]

\[
d\sigma/d\Omega = \frac{(4\pi)^2}{k^2} |A(n)|^2 \sin^2 \delta.
\]

The second step of the method is, if necessary, an evaluation of the partial wave for the system of NPs. For this purpose the equation (3) is integrated numerically with account the behavior at infinity (2), which is already known. After that the partial wave is written as the linear combination (1) of atomic waves \(\Phi_{ilm}(r)\). Further the perturbation theory can be applied. Methods of perturbation theory (for example MP2 [18]) were found good for molecular states calculations, it allows to expect to achieve good results by rather simple scheme.

III. EXAMPLE OF URACIL

As an illustration, we consider low energy electron-molecule scattering for uracil molecules. The computational steps involved in our calculation can be summarized as follows.

(i) Choice of target basis and eigenstates. We restrict our consideration to the fixed-nuclear approximation and assume that ground molecular state remains unperturbed during the scattering. The single-determinant molecular wave function (in basis set 6-31G(d)) and static potential were obtained in ab initio calculation with quantum chemistry package.
(ii) **Choice of effective radii.** To compute NPs we divide all space to non-overlapping areas $|r - a_i| \leq d_i$ corresponding to separate atoms with effective radii $d_i$. In order to evaluate the atomic radii $d_i$ we used the bond lengths, which were obtained using a geometry optimization procedure, and the following equations

$$d_i + d_j = |a_i - a_j|.$$ 

The effective radii are listed in Table I.

(iii) **Choice of NPs.** To avoid the computational complexity related with coupling terms, we average static interaction over angles and compute the radial NPs which were expressed in the following form

$$V_{st}(r) = -\frac{q(r)}{r}, \quad r \leq d$$

where $q(r)$ denote effective charges. Our calculations show that $q(r)$ is smooth function. Calculated static potential are plotted in Figure 1. To include the nonlocal exchange interaction we used local density approximation, originally proposed by Slater [19, 20] for atomic problems. Further the approximation of the local potential was applied to scattering problems [21, 22, 23] and calculating molecular quantum defects for small closed-shell target molecules [24]. In the paper of Hara [23] the following effective potential, depending on energy of impact electron is introduced

$$V_{ex}(r) = -\frac{2}{\pi} k_F(r) \left( \frac{1}{2} + \frac{1 - \eta^2}{4\eta} \ln \left| \frac{1 + \eta}{1 - \eta} \right| \right),$$

(8)

where $k_F(r) = \left[ 3\pi^2 \rho(r) \right]^{1/3} -$ Fermi momentum, and $\rho(r)$ denotes averaged (over angles around the atom) electron density. These densities were obtained in ab initio calculation via density matrix. The parameter $\eta$ is given by the equality

$$\eta = \left[ k^2 + 2I + k_F^2(r) \right]^{1/2} / k_F(r),$$

(9)

where $I$ - molecule ionization energy (in a.u.). The equation (9) emerges from the assumption that the scattered electron and the electron in the highest energy bound state (i.e. Fermi electron, which has momentum $k_F(r)$) move in the same potential field. For the uracil molecule the experimental value of the ionization energy is estimated as $I = 8.35$ eV. The exchange Hara’s potential (8) is attractive (at arbitrary $k$), because the expression in brackets is always positive. When the scattering electron energy ($k^2/2$) grows, the expression at the bracket uniformly decrease, that qualitatively in accordance with the this about decreasing with energy contribution of exchange integral.

(iv) **Computation of partial shifts.** To obtain the partial shifts $\delta_{il}$, we solved numerically the radial Schrödinger equation with the potentials, which were obtained from step (iii). The partial shifts were calculated for angular momenta $l = 0, 1$ and are ploted in Figure 2.

(v) **Computation of the matrices S and N.** These matrixes (for every irreducible representations) were constructed by the formulas (5) and (6).

(vi) **Computation of $\delta$ and $\sigma$.** Using the matrix elements assembled from step (v), the molecular partial shifts were calculated from eigenvalue problem (2) using Cholesky decomposition. The results of the computations at different energies are summarized in Figures 3 and 4. The integral cross section, averaged over molecular orientations, were found by formula $\sigma = (4\pi/k^2) \sum \sin^2 \delta$. The integral cross sections are plotted in Figure 5.

(vii) **Computation of resonances.** The resonance positions and widths were found via the equations

$$\delta(E) = \pi/2, \quad \Gamma = 2\delta'(E)^{-1}$$

and are listed in Table II.
The Figure 5 shows that resonance positions (2.16, 5.16, 7.8 eV) found in $R$-matrix calculations [2] agree with our calculations. The sharp peak at 2.2 eV in Figure 5 may also arise from long-lived anion state, whose lifetime is sufficiently long to allow nuclear motion and, as consequence, possible fragmentation. Indeed, recent experiments [25, 26] showed effective destruction of uracil through dissociative electron attachment (DEA). Also a large peak around 1.0 eV was observed. In Ref. [26] authors explain that the sharp peak, in their DEA measurements, can be associated with vibrational Feshbach resonance, that is, exited vibrational levels of the dipole bound anion states of these compounds. In should be noted, that we exclude (for simplicity) dipole interaction. Thus, our sharp peak indicates another possible explanation, which, however, does not exclude the arguments of Ref. [26].
### TABLE II: Resonance parameters.

| Symmetry | $E_{\text{res}}$ (eV) | $\Gamma$ (eV) |
|----------|---------------------|--------------|
| $A'$     | 1.2                 | 1.1          |
|          | 2.2                 | 0.3          |
|          | 6.7                 | 1.5          |
| $A''$    | 1.9                 | 4.4          |
|          | 5.6                 | –            |
|          | 6.1                 | –            |

**FIG. 5:** Cross sections as functions of incident electron energy. Solid line: our integral cross sections; upper points: partial cross sections with the symmetry $A'$; lower points: partial cross sections with symmetry $A''$.

**IV. CONCLUSION**

We have discussed the "multiple-scattering" method emerged from the zero-range and muffin-tin theories. The method reduces electron-molecule scattering to generalized eigenvalue problem (7) for hermitian matrices. A noteworthy feature of the method is direct possibility to calculate the wave functions (partial waves). This way is based on one-dimensional inhomogeneous Schrödinger equation (3) for radial component $\psi_{ilm}(r)$ and only requires the atomic potential and partial phase of given partial wave. Thus, this approach may be especially important in relation to Bardsley-Fano theory [27, 28] and dissociative attachment at low energies.

The preliminary results on uracil presented here are quite promising. Particularly, our positions of the shape resonances demonstrate good agreement with the $R$-matrix calculations [2]. Thus, this method can be applied to another DNA bases, such as adenine, cytosine, thymine etc. In this connection, it is interesting and important to extend the method to the case of long range interactions, such as dipole interactions. Note, this method gives fast numerical scheme and, therefore, we have good base for future approximations and modeling of electron-DNA scattering in sense of the works [29].

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