

## Low-Energy Electron Diffraction and Resonances in DNA and other Helical Macromolecules

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We propose a framework to calculate the intermolecular multiple elastic scattering of low-energy electrons from helical macromolecules and indicate how it affects the resonant capture cross section. Using a model of DNA, an appreciable enhancement of the elastic and resonant capture cross sections is predicted at incident energies below 15 eV. These results may qualitatively explain the observed prominence of low-energy resonances in strand breaking of plasmid DNA.

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Recent technological advances have rendered possible measurements of low-energy electron scattering and attachment processes in large biological molecules such as DNA [1–4]. Both in single oligonucleotides [5,6] and double stranded DNA [1–3], it has been shown that low-energy electrons (LEE,  $E < 15$  eV) can cause considerable damage via the dissociation of specific basic molecular units [3,4,7,8] of these molecules. Such damage was found to be strongly influenced by electron resonances [1,4–6]. For example, most of the single and double strand breaks induced by LEE can be related to the formation of transient anions of basic subunits of DNA (e.g., the bases and sugar analogs) and their decay into the electronic excitation and/or the dissociative electron attachment (DEA) channels [7,8]. In contrast to known electronic excitation and ionization cross sections [9], the effective cross sections for these strand breaks at the resonance energies ( $\sim 10$  eV) are about of the same magnitude as at 50 eV [2]. This is surprising since at 50 eV there are many more dissociative neutral and ionic states which could break bonds within DNA. Furthermore, some of the electrons produced by ionization at 50 eV could also damage DNA.

Even though reasonably successful theories have been proposed to explain the behavior of electron-molecule scattering at low energies, no suitable framework presently exists to treat the scattering problem with a molecule that may contain up to  $10^{10}$  atoms. As such this number is too large for a solution with density functional theory [10], which in any case, is presently limited to electrons interacting with a limited number of ground state molecules (recent extensions to a few thousand atoms are now possible [11,12], but the scattering aspects have not yet been addressed). Thus, the description of the behavior of the cross sections for electron scattering from large biomolecules at low energies poses a challenge to the theory. In this Letter, we propose a new framework to describe theoretically LEE scattering from large biomolecules. Inspired by the physics in the  $R$ -matrix theory [13] and the work of O'Malley [14,15], we decouple the problem into two parts: first the electron interacts with

the entire molecule and then the new wave function, defined by the atomic arrangement within the molecule, interacts at a specific site of the molecule (e.g., a basic subunit). There are two reasons for this choice: electron attachment requires the localization of the electron on a small subunit of the biomolecules and an electron of energy typically 5–15 eV has a wavelength that is of the order of molecular and intermolecular distances and is thus delocalized. It is then likely to undergo multiple scattering before interacting at a specific site, where it can be captured in a resonant state. The idea of decoupling the diffracted amplitude from the final local site interaction has recently been successfully applied by Fabrikant and co-workers [16,17] in describing with  $R$ -matrix theory the behavior of the absolute cross section for DEA to small molecules embedded in a rare gas matrix. In this case, scattering separates into two regions: inside the  $R$ -matrix sphere, where the matrix elements are those of the gas phase modified by the condensed phase, and outside the sphere, where the interaction with the rare gas atoms is dominant, causing electron diffraction which modifies the vacuum electron wave function.

In this paper, we first address the multiple scattering problem and then attempt to connect it to local resonant capture. In a helical macromolecule, such as DNA, the angular twist in the sequence of rungs (the base pairs of DNA and their sugar-phosphate partners) is a fundamental geometrical property which is of crucial importance to the diffraction process. We thus propose a study of the interference produced by a helical structure. We show that with the present formulation, the energy dependence of the electron wave function inside DNA and similar helical macromolecules can be obtained with minimal computer time, and the diffraction of the electron wave may explain qualitatively the large contribution of electron resonances to DNA damage below 15 eV.

We propose a simple model of molecular subunits (i.e., bases, sugars, and phosphates) immersed in an optical potential  $U_{op}$ , which is constant between their  $R$ -matrix shells, a working hypothesis used in the calculations for simple molecules [18] and in the theory of low-energy

electron diffraction in solids [19] (between the muffin tins). One can quite generally describe the scattering problem of a molecule by its scattering matrix  $S_{LL'}$  [20,21]. This matrix has thus far been calculated for fairly complex molecules such as benzene [22,23] and calculations for DNA bases are probably impending. More specifically, the asymptotic form outside the  $R$ -matrix shell of the total wave function for an incident plane wave of momentum  $\vec{k}$  on a molecule centered at  $\vec{R}_n$  is given by the following equation:

$$\psi_{\vec{k}}^{(n)}(\vec{r}) = 4\pi e^{i\vec{k}\cdot\vec{R}_n} \sum_{LL'} i^l Y_L^*(\Omega_{\vec{k}}) Y_{L'}(\Omega_{\vec{r}_n}) \times \left[ j_l(kr_n) \delta_{LL'} + \frac{1}{2} (S_{LL'}^{(n)} - \delta_{LL'}) h_{l'}^+(kr_n) \right]. \quad (1)$$

We use the compact notation  $L = (l, m)$  and  $\vec{r}_n = \vec{r} - \vec{R}_n$ . In the environment of a macromolecule, each molecular subunit has the incident plane wave impinging on it plus the scattered waves of all other subunits:

$$\psi_{\vec{k},i}^{(n)}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} + \sum_{n' \neq n} \psi_{\vec{k},s}^{(n')}(\vec{r}). \quad (2)$$

Equation (1) then generalizes to

$$\psi_{\vec{k}}^{(n)}(\vec{r}) = 4\pi e^{i\vec{k}\cdot\vec{R}_n} \sum_{LL'} i^l B_{\vec{k}L}^{(n)} Y_{L'}(\Omega_{\vec{r}_n}) \times \left[ j_l(kr_n) \delta_{LL'} + \frac{1}{2} (S_{LL'}^{(n)} - \delta_{LL'}) h_{l'}^+(kr_n) \right], \quad (3)$$

where

$$B_{\vec{k}L}^{(n)} = A_{\vec{k}L}^{(n)} + Y_L^*(\Omega_{\vec{k}}),$$

and  $A_{\vec{k}L}^{(n)}$  is the incoming contribution from all other molecules. When we expand  $\sum_{n' \neq n} \psi_{\vec{k},s}^{(n')}(\vec{r})$  around  $\vec{R}_n$  [18,24], we find

$$A_{\vec{k}L}^{(n)} = \frac{1}{2} \sum_{n' \neq n} \sum_{L_1, L_2, L'_2} i^{l_1+l_2-l'_2} B_{\vec{k}L_2}^{(n')} (S_{L_2 L'_2}^{(n')} - \delta_{L_2 L'_2}) (-1)^{m'_2} \times e^{-i\vec{k}\cdot\vec{R}_{nn'}} F_{m_1, m_2, -m'_2}^{l_1, l_2, l'_2} Y_{L_1}(\Omega_{\vec{R}_{nn'}}) h_{l_1}^+(kR_{nn'}), \quad (4)$$

where

$$F_{m_1, m_2, m_3}^{l_1, l_2, l_3} = [4\pi(2l_1+1)(2l_2+1)(2l_3+1)]^{1/2} \times \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix},$$

$\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$  is the Wigner 3- $j$  symbol [25], and  $\vec{R}_{nn'} = \vec{R}_n - \vec{R}_{n'}$ . Equation (4) implies a coupled set of linear equations for all  $B_{\vec{k}L}^{(n)}$ . This would prove arduous if not impossible were it not for the loss of coherence of the electrons due to inelastic collisions and to parasite scatterers (the structural water molecules in the grooves could be considered as such). These processes can be invoked through an imaginary part in the background optical potential  $U_{op}$  [19], i.e., an imaginary part to the electron wave number

$\text{Im}(k) = \xi^{-1}$ . Here  $\xi$  acts as a coherence length for the electrons. This allows approximate though accurate local solutions by truncated finite-size matrices containing the information for the number of subunits within a few coherence lengths.

Once the elastic scattering problem is solved, the resonant capture cross section  $\sigma_{rc}$  of a subunit can in principle be obtained from Eq. (2). The  $R$ -matrix approach [13,26], which has successfully been used in solids [16,17], could be used to calculate  $\sigma_{rc}$  by matching the wave function on the  $R$ -matrix boundary shell. The theory would have to be adapted, however, to a nonspherical shell in view of the nearly planar shape of the bases and the proximity of subunits in the neighboring rungs (base pairs) of the helix. The formalism of O'Malley [14,15] can be more practical at this point. The basic electronic matrix element that couples the external wave function to the internal resonance state for an incident plane wave is given by the capture amplitude which can be written in general terms as  $V_{\vec{k}} = \sqrt{4\pi} \sum_L V_L Y_L^*(\Omega_{\vec{k}})$ . The resonant component of the capture cross section resides in the nuclear part of the  $t$  matrix. Looking at Eq. (3), it is seen that this result can be simply generalized to

$$V_{\vec{k}}^{(n)} = \sqrt{4\pi} \sum_L V_L B_{\vec{k}L}^{(n)} e^{i\vec{k}\cdot\vec{R}_n} \quad (5)$$

for the subunit at  $\vec{R}_n$ .

We now wish to illustrate this procedure by specializing our theory to a helical macromolecule made of repeating rung units of pseudomolecules (PMOL) that are constructed from identical centrosymmetric scatterers as shown in Fig. 1. This structural regularity is not required by the theory but it greatly simplifies the calculations. We now let the sum over  $n$  in Eq. (4) run over the individual scatterers. Moreover, for single centrosymmetric scatterers, one has  $\frac{1}{2}(S_{LL'}^{(n)} - \delta_{LL'}) = \delta_{LL'} e^{i\delta_{nl}} \sin(\delta_{nl})$  where  $\delta_{nl}$  is the  $n$ th scatterer phase shift.

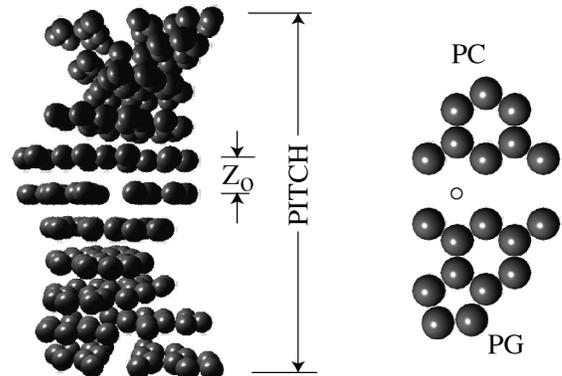


FIG. 1. The basic pseudomolecular PC-PG unit, defining a rung, is shown on the right. The open circle marks the position of the helix's rotation axis. The helical structure obtained by applying the screw operation to the PC-PG unit appears on the left (not to scale) showing parameters defined in the text.

We have used the following parameters: a screw pitch of  $c = 3.4$  nm and a number of residues per turn  $N_c = 10$  which are characteristic of the B form of DNA [27], the  $l = 0, 1, 2$  phase shifts of the electronically inert species argon [28], a value of the wave function coherence length of 20 Bohr radii, that is  $\xi = 1.06$  nm. This value is representative of solids [19,28] and biological materials [2]; furthermore, it compensates for the regularity of our helix. We have constructed two PMOLs. These are PC and PG of Fig. 1 built around hexagonal rings having the interscatterer distance of benzene [22], 0.14 nm, and a center-to-center distance of 0.56 nm. This ring structure is fundamental to the structure of the DNA bases [27]. It bears resemblance to the central part of the C-G base pairing in the B-DNA decamer of Ref. [29]. Finally, we have chosen the incident direction to be perpendicular to the axis of helix. This choice is suggested by the experimental conditions [1,2,30,31] in which impinging electrons are normal to the films and thus predominantly perpendicular to the DNA strands which are expected to lie mostly in the plane of the films. Incidentally, we find that the elastic scattering cross section of a single ring in a lossless medium ( $\xi = \infty$ ), using the phase shifts of argon, is of the same magnitude as that of benzene [22,23].

We calculated the elastic cross section per turn  $\sigma_e$  for our model helix. It is defined as the ratio of the radial outward-scattered current to the incident flux. This is shown in Fig. 2 which compares the cross section for the helix to that of independent rungs (multiple scattering between rungs turned off). The enhancement due to multiple scattering is substantial. All other things being equal, it is the wave function amplitude  $B_{\vec{k}L}^{(n)}$  which makes the difference. It is increased by multiple scattering. Diffraction patterns are also apparent in Fig. 2. Interestingly, an iterative solution to Eq. (4) in terms of the inter-rung scattering processes is not convergent for our choice of parameters. There is no meaningful intermediary between the independent-rung limit and the global solution. The subunits are quite effectively intercon-

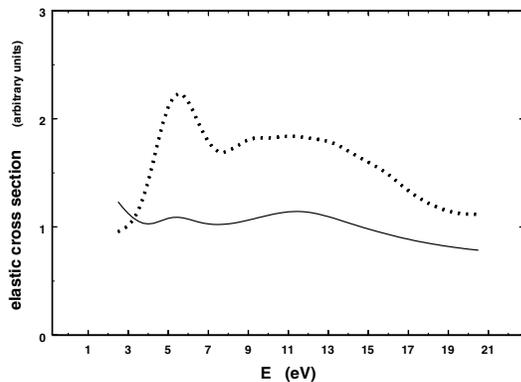


FIG. 2. Elastic cross section for the model helix, dashed line, compared to the independent-rung limit, full line.

nected through multiple scattering and are thus sensitive to the axial geometry.

The estimation to  $\sigma_{rc}$  of a PMOL goes through the evaluation of the capture amplitude. Expanding Eq. (2) around the center  $\vec{R}_c$  of the PC ring for instance, we find

$$\begin{aligned} \psi_{\vec{k},i}^{\text{PC}}(\vec{r}) &= e^{i\vec{k}\cdot\vec{r}} + \sum_{n' \notin \text{PC}} \psi_{\vec{k},s}^{(n')}(\vec{r}) \\ &= 4\pi e^{i\vec{k}\cdot\vec{R}_c} \sum_L i^l [C_{\vec{k}L} + Y_L^*(\Omega_{\vec{k}})] Y_L(\Omega_{\vec{r}_c}) j_l(kr_c), \end{aligned} \quad (6)$$

$$\begin{aligned} C_{\vec{k}L} &= \sum_{n' \notin \text{PC}} \sum_{L_1, L_2} i^{l_1+1} B_{\vec{k}L_2}^{(n')} e^{i\delta_{n'l_2}} \sin(\delta_{n'l_2}) (-1)^{m_2} e^{-i\vec{k}\cdot(\vec{R}_{cn'})} \\ &\times F_{m_1, m_2}^{l_1, l_2} Y_{L_1}(\Omega_{\vec{R}_{cn'}}) h_{l_1}^+(kR_{cn'}). \end{aligned} \quad (7)$$

Equation (5) now becomes

$$V_{\vec{k}}^{(c)} = \sqrt{4\pi} \sum_L V_L [C_{\vec{k}L} + Y_L^*(\Omega_{\vec{k}})] e^{i\vec{k}\cdot\vec{R}_c}. \quad (8)$$

We obviously need to make some sort of approximation in order to extract information about trends. We shall use the one-center approximation of O'Malley [15] and assume that there is a dominant capture channel symmetry corresponding to  $V_{L_0}$ . We calculate the square of the corresponding capture amplitude relative to the situation with multiple scattering turned off

$$\begin{aligned} \Gamma_{\text{rel}}(L_0) &= |\sqrt{4\pi} V_{L_0} [C_{\vec{k}L_0} + Y_{L_0}^*(\Omega_{\vec{k}})] e^{i\vec{k}\cdot\vec{R}_c}|^2 \\ &\div |\sqrt{4\pi} V_{L_0} Y_{L_0}^*(\Omega_{\vec{k}}) e^{i\vec{k}\cdot\vec{R}_c}|^2. \end{aligned} \quad (9)$$

We propose to look at different cases associated with predominantly planar,  $(l_0, m_0) = (3, 3), (4, 4), (5, 5), (6, 6)$ , and predominantly axial entry channels,  $(l_0, m_0) = (3, 1), (4, 0), (5, 1), (6, 0)$ , which are to be associated with various subunit symmetries. We consider only situations with  $l_0 + \mu_0 = \text{even}$ , for which  $Y_{l_0, \mu_0}^*(\Omega_{\vec{k}}) \neq 0$ , given our choice of  $\vec{k}$  perpendicular to the helix axis. The results appear in Fig. 3. For each value of  $l$ , we have chosen to plot only the interval of energy in which a resonance is most likely to be found given the resonance energies for benzene [22,23]. The axial piling of subunits is seen to favor the axial capture channels. The enhancement is appreciable. This behavior prevails for the various other PMOL configurations we have tried.

We can now understand that  $\sigma_e$ , of Fig. 2, is enhanced predominantly by the axially redistributed electrons which constructively superimpose with the incident plane wave on the molecules.

In conclusion, the resonant capture cross section will be roughly that of a freestanding molecule if the dominant capture channel, for incident electron momentum  $\vec{k}$  in the plane of the molecule, is planar (large  $|m|$ ). One should expect enhancements in the resonant capture cross sections for axially important capture channels. This result

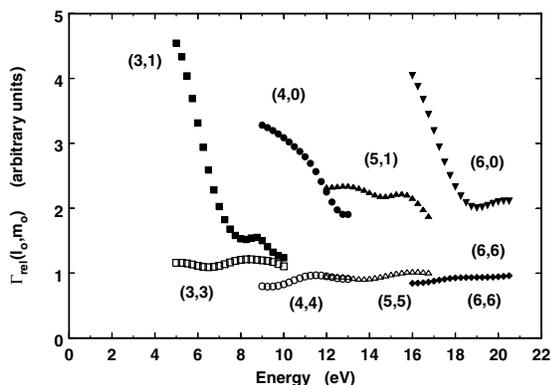


FIG. 3. Square of the capture amplitude relative to the free-standing situation, Eq. (9), at the center of the PC ring in physically significant electron energy intervals relative to  $\text{Re}(U_{op})$ . Various one-center entrance channels, identified by their angular momenta  $(l_0, m_0)$ , are shown.

may qualitatively explain the dominance of electron resonances observed in the damage to DNA induced by LEE [1,2,4]. A similar behavior is expected for other helical macromolecules. More generally, the present formulation indicates that the LEE resonance scattering problem on a macromolecule can be solved theoretically by taking the diffracted elastic intensity inside this molecule as the captured wave.

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