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On the Calculation of Biomolecular Mean Excitation Energies

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Biological damage resulting from exposure to radiation results from either single (SSB) or double (DSB) strand breaks in DNA. Relatively few such breaks are produced by direct hits of ions on DNA, most damage being done by fragmentation products of water. Understanding the interaction of massive radiation, such as protons or alpha particles, with biological targets, including water, becomes increasingly important as we seek to protect healthy cells from radiation damage.

The problem of describing and explaining the effects of radiological action on biological systems is tremendous, [1,2] as the problem extends over many orders of magnitude in complexity, time scale, and size. In any such process, where there is exposure of a biological entity to radiation, there are long chains of sequential and parallel actions, as well as possible non-linearities between initial radiations induced molecular changes and final biological effects [3]. The chain of events begins with the initial interaction of the radiation with a biomolecule, and it is this initial process that is considered here. This is done by applying quantum mechanical molecular electronic structure theory to the problem.

Massive particles (ions) deposit energy in a molecule by collision with either the electrons, the dominant mechanism at higher collision energies, or with the nuclei of the molecule, which is more important at lower collision energies. In either case, the collision typically results in electronic excitation of the target molecule, followed by ionization, decay, emission of secondary radiation, and/or fragmentation. In the case of a swift ions colliding with a biomolecule, the energy deposition is done predominantly at the end of the ion's track through the target just before the particle comes to rest.

Perhaps the most spectacular form of radiation, due to the large amount of energy that it can deposit in matter, comes from impact of highly charged, high energy heavy ions (e.g. Xe^{18+}) with biomaterials. Most ionic radiation is not so spectacular, however, and consists of swift protons and alpha particles. These particles also ionize and fragment water as well as causing damage by direct hits on a biomolecule.

Consider the very first steps in the energy deposition by a fast ion colliding with a biomolecule. The single materials parameter that best describes the energy transfer from the projectile to the target, called the ion stopping power of the target molecule, is the mean excitation energy (*vide infra*) of the target, and that is the quantity that we focus on here.

The simplest quantum mechanical treatment of energy transfer by a fast ion of mass M and charge +Ze to a target atom or molecule is that of Bethe [4] which we consider here.

Energy transfer to a molecule by a fast ion is frequently described in terms of the so called linear energy transfer (LET), or stopping power $-dE/dx$, of the target molecule [5,6]. To avoid problems when comparing stopping in targets of different densities, one frequently considers the stopping cross section $S(v)$:

$$-\frac{dE}{dx} = N\,S(v) \tag{1}$$

Where N is the number density of the scatterers, and v is the projectile velocity. The cross section is derived by standard time-dependent perturbation theory [7].

Expanding the time-dependent and employing the machinery of time-dependent perturbation theory, yields the differential cross section $\sigma_n(q)dq$ as function of the momentum transfer q. The differential cross section is essentially the number of ions experiencing a momentum transfer $q = |\vec{q}| = |\vec{k} - \vec{k}_n|$ in the inelastic scattering while leaving the molecule in the excited state $|\Psi_n\rangle$ with energy E_n. The total cross section is obtained by summing over all excited electronic states of the molecule, bound as well as continuum states, and integrating over all possible values of the momentum transfer q.

$$-\frac{dE}{dx} = N \int_{q_{\min}}^{q_{\max}} \sum_{n>0}^{\text{bound}} (E_n - E_0)\sigma_n(q)dq \tag{2}$$

Finally, carrying out the summation and integration and comparing the result to equation (2), one obtains the Bethe expression for the stopping cross section:

$$S(v) = \frac{4\pi e^4 Z^2 N_e}{m_e v^2} \ln \frac{2m_e v^2}{I_0} \tag{3}$$

where the quantity I_0 is known as the mean excitation energy of the target, and is defined as the first energy weighted moment of the dipole oscillator strength distribution (DOSD) of the target

$$\ln I_0 = \frac{\sum_{n>0} f_{0n} \ln(E_n - E_0)}{\sum_{n>0} f_{0n}} \tag{4}$$

Here the summation is over transitions from the ground state to all bound excited states n having energy E_n and with dipole oscillator strength f_{0n}, and integration over all excited continuum states of the target molecule.

Inokuti pointed out [8] that "The mean excitation energy, I_0, is the sole nontrivial property of matter appearing in Bethe's expression for the stopping power for a charged particle at high speed". The mean excitation energy measures the difficulty with which a target molecule can absorb energy from a massive projectile. Large mean excitation energies correspond to greater difficulty for the absorption of energy by a target molecule, and thus lead to lower stopping power. We will thus concentrate on the mean excitation energies of the biomolecules as descriptors of their interaction with swift ions.

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In this simplest version of stopping theory according to Bethe [4] it is assumed that the projectile velocity v is considerably larger than the velocity of the electrons in the target molecule. In order to extend the treatment to the case of smaller projectile velocity, equation (3) can be generalized to

$$S(v) = \frac{4\pi e^4 Z^2 N_e}{m_e v^2} L(v) \tag{5}$$

where the stopping number, $L(v)$, is extended by so-called shell corrections, $-\frac{C(v)}{N_e}$, i.e.

$$L(v) = \ln \frac{2m_e v^2}{I_0} - \frac{C(v)}{N_e} \tag{6}$$

Which approach zero for increasing projectile velocities.

The vertical electronic excitation energies, $E_n - E_0$, and associated electronic transition dipole moments for a molecule that are needed in order to obtain the mean excitation energies according to equation (4) can conveniently be extracted from the linear response function or polarization propagator [9].

This approach yields a finite number of excitations. As a result, the integrations over the continuum states in equation (4) are done numerically using the excitation energies with energies larger than the first ionization energy of the system, called pseudo-states, as integration points. We have found that this discretization of the continuum works well provided sums over the entire excitation spectrum are taken [10]. The DOSD sum rules and mean excitation energies in equation (4) are then obtained by explicit summation of the oscillator strengths to all bound states and to the discrete continuum pseudo-states. Experience indicates that about 12% of the mean excitation energy is due to excitation to bound states, while the remaining 88% comes from transitions into the pseudo-states for the biomolecules we have considered.

Experience also shows [11] that some amount of electron correlation is needed in order to calculate reliable spectral moments of the DOSD. One needs to calculate the propagator at least at the level of the time-dependent Hartree-Fock, also called the random phase approximation (RPA), [12,13] which implies using a Hartree-Fock self-consistent field wave function as the function the linear response of which we are calculating. The RPA adds correlation in both ground and excited states in a balanced way [14]. Alternatively time-dependent density functional theory (TD-DFT) [15-17] can successfully be employed in the calculation of DOSDs and thus mean excitation energies.

This scheme has been quite successful fin the study of the interaction of fast ions with biomolecules [18].

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