Noncharacteristic Radiations in Atomic and Molecular Collisions*

J. C. Y. Chen and T. Ishihara
Department of Physics, University of California, San Diego, La Jolla, California 92037

and

K. M. Watson
Department of Physics, University of California, Berkeley, California 94720
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Noncharacteristic radiations in atomic and molecular collisions are examined. A new mechanism is considered in which electrons are induced to radiate collectively. The collective radiations are present even in the absence of inner-shell vacancies. The importance of this mechanism increases with collision energy and the number of electrons. The emitted photon energy increases with collision energy and can exceed the united-atom limit. The asymmetries of the noncharacteristic radiation are examined.

Recently, it has been proposed that the observed noncharacteristic x rays in ion-atom collisions are due to transitions between quasimolecular states of the colliding system.[1] Because of the parametric dependence of the electronic (quasimolecular) states on the nuclear separation $\vec{R}$ and the coupling of the nuclear motion with the radiation field, the electronic motion can be induced to radiate during collisions. Theoretical treatments of such induced radiations were carried out by Müller and Greiner.[2] They attributed the observed radiations to come from spontaneous and (rotationally) induced electric-dipole transitions to inner-shell vacancies. Noncharacteristic x rays have now been observed for a number of systems.[3]

In this communication, we would like to propose an additional mechanism for the noncharacteristic radiations, namely collective electron radiations. During the collision, electrons can be induced to radiate collectively because of the distortion of the charge densities and the coupling of the radiation field with the nuclear motion. Radiations of this latter type are present even in the absence of inner-shell vacancies. The importance of this mechanism increases with collision energy and number of electrons.

Following Müller and Greiner, we shall treat the nuclear motion classically but neglect the relativistic effects in the electronic motion since the latter are not essential in illustrating the above mentioned mechanism. We notice that the matrix elements for the induced radiation do not in general vanish at R values where the quasimolecular states merge into the separated-atomic states. Care is therefore made in removing the spurious contributions. We also found that the spontaneous radiations coming from the quasimolecular electric dipole are not uniformly distributed (even for closed shells). This is of importance in analyzing the observed directional anisotropy of quasimolecular radiation.

We assume that the collision system is governed by

$$i\hbar\,\partial\Psi/\partial t=[H_e(\vec{r},\vec{R})+H_r(\vec{r},\vec{R})+H_N]\Psi, \tag{1}$$

where $\vec{r}$ denotes the collection of electronic coordinates $\vec{r}_i$, H_e is the adiabatic electronic Hamiltonian, H_N is the free-field Hamiltonian, and H_r is the interaction with the radiation field. We have[4]

$$H_r=\sum_{\vec{k}}\sum_{\lambda=1}^{2}\Big(\sum_i[\vec{A}_{\vec{k}\lambda}(\vec{r}_i)b_{\vec{k}\lambda}+\vec{A}_{\vec{k}\lambda}{}^*(\vec{r}_i)b_{\vec{k}\lambda}{}^\dagger]\cdot\vec{p}_i\Big), \tag{2}$$

with

$$\vec{A}_{\vec{k}\lambda}(\vec{r}_i)=\frac{1}{L^{3/2}}\left(\frac{e}{mc}\right)\left(\frac{2\pi\hbar c}{k}\right)^{1/2}\hat{e}_{\vec{k}\lambda}\exp(i\vec{k}\cdot\vec{r}_i), \tag{3}$$

where $\vec{A}_{\vec{k}\lambda}$ is the vector potential associated with a photon of energy $\hbar\omega(=\hbar ck)$ and polarization unit vector $\hat{e}_{\vec{k}\lambda}$ propagating in the direction defined by the wave vector $\vec{k}$.

The quasimolecular states φ_α ($H_e\varphi_\alpha=\mathcal{E}_\alpha\varphi_\alpha$) are expressed in the molecular coordinate system with

$\hat{z}'$ taken to be $\hat{R}$. At large R values, φ_α does not merge into separated-atomic states $g_\alpha(\vec{r})$ in the space-fixed coordinate system with $\hat{z}$ taken to be $\hat{V}$, the incident beam direction. Instead, we have $\varphi_\alpha(\vec{r}', \vec{R}) \rightarrow g_\alpha'(\vec{r}')$, where the prime on g_α and $\vec{r}$ serves to remind us of the molecular coordinate system. The use of states φ_α, photon states $|N_{\vec{k}\lambda}\rangle$ $[H_N|N_{\vec{k}\lambda}\rangle = \hbar\omega N_{\vec{k}\lambda}|N_{\vec{k}\lambda}\rangle]$, and the expansion

$$\Psi = \sum_{\alpha N_{\vec{k}\lambda}} \mathfrak{a}_{\alpha N_{\vec{k}\lambda}}(t)\varphi_\alpha(\vec{r}', \vec{R})|N_{\vec{k}\lambda}\rangle,$$

(translational factors are neglected) transforms Eq. (1) into

$$i\dot{\mathfrak{a}}_{\alpha N_{\vec{k}\lambda}} = \mathcal{E}_{\alpha N_{\vec{k}\lambda}}\mathfrak{a}_{\alpha N_{\vec{k}\lambda}} + \sum_{\beta, N_{\vec{k}\lambda}'} v_{\alpha N_{\vec{k}\lambda}, \beta N_{\vec{k}\lambda}'}\mathfrak{a}_{\beta N_{\vec{k}\lambda}'}, \tag{4}$$

with

$$v_{\alpha N_{\vec{k}\lambda}, \beta N_{\vec{k}\lambda}'} = i\langle\varphi_\alpha|\dot{\varphi}_\beta\rangle\delta_{N_{\vec{k}\lambda}N_{\vec{k}\lambda}'} + \sum_{\vec{k}}\sum_\lambda\{\langle\varphi_\alpha|\sum_i \vec{A}_{\vec{k}\lambda}^*(\vec{r}_i)\cdot\vec{p}_i|\varphi_\beta\rangle N_{\vec{k}\lambda}^{1/2}\delta_{N_{\vec{k}\lambda}, N_{\vec{k}\lambda}'+1}$$
$$+\langle\varphi_\alpha|\sum_i \vec{A}_{\vec{k}\lambda}(\vec{r}_i)\cdot\vec{p}_i|\varphi_\beta\rangle(N_{\vec{k}\lambda}+1)^{1/2}\delta_{N_{\vec{k}\lambda}, N_{\vec{k}\lambda}'-1}\}, \tag{5}$$

where $\mathcal{E}_{\alpha N_{\vec{k}\lambda}} = \mathcal{E}_\alpha + \hbar\omega N_{\vec{k}\lambda}$ and $\langle\varphi_\alpha|\dot{\varphi}_\beta\rangle$ are the nonadiabatic interactions due to the coupling of the electronic motion with the nuclear motion.

The radiation field is coupled with the nuclear motion through the electron velocities $\vec{v}_i$. To exhibit this coupling we may make use of the time dependence of $\vec{R}$ and write

$$d/dt = (\partial/\partial t)_R + \{(d\vec{R}/dt)\cdot\nabla_{\vec{R}}\}_{\text{space fixed}};$$

we then obtain, writing $d\vec{R}/dt = \vec{V}$,

$$\vec{v}_i = d\vec{r}_i/dt = \vec{p}_i'/m + \vec{\Omega}\times\vec{r}_i' + (\vec{V}\cdot\hat{R})\vec{r}_i'/R, \tag{6}$$

where we made use of the transformation of $\nabla_{\vec{R}}$ in the space-fixed system to the molecular system. In Eq. (6), $\vec{p}_i'/m$ are the intrinsic electron velocities at a fixed R in the molecular coordinate system, $\vec{\Omega}\times\vec{r}_i'$ are the induced electron velocities through the rotational nuclear motion considered by Müller and Greiner,[2] and $(\vec{V}\cdot\hat{R})\vec{r}_i/R$ are the induced electron velocities through the radial nuclear motion. The coupling of the latter induced electron velocity with the radiation field was not considered previously.

The matrix elements

$$\langle\varphi_\alpha(\vec{r}', \vec{R})|\sum_i\{[(\vec{V}\cdot\hat{R})/R]\vec{A}_{\vec{k}\lambda}\cdot\vec{r}_i' + \vec{A}_{\vec{k}\lambda}\cdot(\vec{\Omega}\times\vec{r}_i')\}|\varphi_\beta(\vec{r}', \vec{R})\rangle$$

for the induced radiations do not vanish in general at R values where φ_α merge into $g_\alpha'(\vec{r}')$. This would give rise to spurious contributions when the expansion of Ψ is not used in its entirety. To avoid this spurious contribution we write $v_\alpha = \mathcal{E}_{\alpha N_{\vec{k}\lambda}} - W_{\alpha N_{\vec{k}N}}$ (with $W_{\alpha N_{\vec{k}\lambda}} = \lim_{R\rightarrow\infty}\mathcal{E}_{\alpha N_{\vec{k}\lambda}}$) and

$$J_{\alpha N_{\vec{k}\lambda}, \beta N_{\vec{k}\lambda}'} = v_{\alpha N_{\vec{k}\lambda}, \beta N_{\vec{k}\lambda}'} - \lim_{R\rightarrow\infty} v_{\alpha N_{\vec{k}\lambda}, \beta N_{\vec{k}\lambda}'}.$$

With the help of the transformation

$$\mathfrak{a}_{\alpha N_{\vec{k}\lambda}} = \sum_\beta\langle g_\alpha'(\vec{r}')|g_\beta(\vec{r})\rangle C_{\beta N_{\vec{k}\lambda}},$$

Eq. (3) can be written as

$$i\dot{C}_{\alpha N_{\vec{k}\lambda}} = W_{\alpha N_{\vec{k}\lambda}}C_{\alpha N_{\vec{k}\lambda}} + \sum_{\beta, N_{\vec{k}\lambda}'}\mathcal{J}_{\alpha N_{\vec{k}\lambda}\beta N_{\vec{k}\lambda}'}C_{\beta N_{\vec{k}\lambda}'}, \tag{7}$$

with

$$\mathcal{J}_{\alpha N_{\vec{k}\lambda}\beta N_{\vec{k}\lambda}'} = \sum_{\alpha'\beta'}\langle g_\alpha|g_{\alpha'}\rangle[v_{\alpha'}\delta_{\alpha'\beta'} + J_{\alpha' N_{\vec{k}\lambda}, \beta N_{\vec{k}\lambda}'}]\langle g_{\beta'}|g_\beta\rangle$$
$$+\sum_{\vec{k}}\sum_\lambda\{\langle g_\alpha|\sum_i\vec{A}_{\vec{k}\lambda}^*\cdot\vec{p}_i|g_\beta\rangle N_{\vec{k}\lambda}^{1/2}\delta_{N_{\vec{k}\lambda}N_{\vec{k}\lambda}'}$$
$$+1+\langle g_\alpha|\sum_i\vec{A}_{\vec{k}\lambda}\cdot\vec{p}_i|g_\beta\rangle(N_{\vec{k}\lambda}+1)^{1/2}\delta_{N_{\vec{k}\lambda}, N_{\vec{k}\lambda}'-1}\}. \tag{8}$$

The first term in the interaction [Eq. (8)] is now expressed in terms of the differences between the quasimolecular states and the asymptotic atomic states. When truncation is made in Eq. (7), each term is free from the spurious contribution. These equations are also free from the unphysical long-range nonadiabatic interactions $i\langle g_\alpha'(\vec{r}')|\dot{g}_\beta'(\vec{r}')\rangle$. This is of importance in the determination of line

broadening due to the radiationless nonadiabatic transitions.[5]

During collisions, the electrons can radiate collectively through the distortion of the charge densities given by the diagonal matrix elements. We have for the induced radiations

$$\int d^3r' \sum_i \exp(i\vec{k}\cdot\vec{r}_i)\{(\vec{\Omega}\times\vec{r}_i') + [(\vec{V}\cdot\hat{R})/R]\vec{r}_i'\}[|\varphi_\alpha(\vec{r}',\vec{R})|^2 - |g_\alpha'(\vec{r}')|^2]. \tag{9}$$

Radiations of this type which have not been previously considered are present even in the absence of inner-shell vacancies. The emitted photon energy should increase with collision energy and can easily exceed the united-atom limit. The leading terms to the matrix elements of Eq. (9) are the quadrupole and magnetic dipole terms. An order-of-magnitude estimation gives for the energy of radiation per collision $\pi^2(V/c)^5Z^2(e^2/a_0)$, where Z is the number of electrons.

The collective radiations arise basically from the induced dipoles created during collision encounters. Let there be N_a and N_b electrons centered at the colliding mass centers a and b, respectively. By the use of the relations $\vec{r}_i' = \vec{r}_{ib}' + \eta_b\vec{R} = \vec{r}_{ia}' - \eta_a\vec{R}$ (where η_a and η_b are mass coefficients with $\eta_a + \eta_b = 1$) and $\vec{V} = (\vec{V}\cdot\hat{R})\hat{R} + \vec{\Omega}\times\vec{R}$, the matrix elements of Eq. (9) can be rewritten as

$$\exp(-i\eta_a\vec{k}\cdot\vec{R})\int d^3r' \sum_i^{N_a} \exp(i\vec{k}\cdot\vec{r}_{ia}')\left[-\eta_a\vec{V} + \vec{\Omega}\times\vec{r}_{ia}' + \frac{\vec{V}\cdot\hat{R}}{R}\vec{r}_{ia}'\right][|\varphi_\alpha(\vec{r}',\vec{R})|^2 - |g_\alpha'(\vec{r}')|^2]$$
$$+ \exp(i\eta_b\vec{k}\cdot\vec{R})\int d^3r' \sum_i^{N_b} \exp(i\vec{k}\cdot\vec{r}_{ib}')\left[\eta_b\vec{V} + \vec{\Omega}\times\vec{r}_{ib}' + \frac{\vec{V}\cdot\hat{R}}{R}\vec{r}_{ib}'\right][|\varphi_\alpha(\vec{r}',\vec{R})|^2 - |g_\alpha'(\vec{r}')|^2].$$

The induced dipoles are seen from the expansion of the first term to be of the forms

$$i\eta_a\vec{V}\vec{k}\cdot\int d^3r' \sum_i^{N_a} \vec{r}_{ia}'[|\varphi_\alpha(\vec{r}',\vec{R})|^2 - |g_\alpha'(\vec{r}')|^2],$$

$$i\eta_a(\vec{k}\cdot\vec{R})\int d^3r \sum_i^{N_a}\left(\frac{\vec{V}\cdot\hat{R}}{R} + \vec{\Omega}\times\right)\vec{r}_{ia}[|\varphi_\alpha(\vec{r}',\vec{R})|^2 - |g_\alpha'(\vec{r}')|^2].$$

Since the induced electron velocities are real [see Eq. (6)], the induced radiations, in the electric dipole approximation, do not interfere with the spontaneous radiations. This allows a possibility of identifying the induced radiation separately from the spontaneous radiation through angular analysis. Müller and Greiner[2] have pointed out that the induced radiations exhibit a strong asymmetry with respect to the beam axis. In their analysis, they took, however, the spontaneous radiations (for closed shells) to be uniformly distributed. Because the quasimolecular dipole depends on the beam direction and the selection rules are derived in the molecular coordinate system, this uniformity is not expected.

The angular dependence of the radiation cross section, differential with respect to the photon energy ω, photon direction $\Omega_{\vec{k}}$, and the scattered beam direction Ω, takes the general form

$$\frac{d^3\sigma}{d\omega\, d\Omega\, d\Omega_{\vec{k}}} \propto |\vec{M}|^2 - |M_x\sin\theta\cos\varphi + M_y\sin\theta\sin\varphi + M_z\cos\theta|^2, \tag{10}$$

where θ and φ are the polar and azimuthal angles of the photon direction with respect to a space-fixed coordinate system (xyz) whose z axis lies along the incident beam direction, and $\vec{M}$ is the appropriate matrix elements. For spontaneous dipole radiations, the M's can be expressed in terms of the dipole matrix elements $\vec{d}_{\alpha\beta}$:

$$\vec{M} \cong \int d^2B \exp(i\vec{q}\cdot\vec{B})\int_{-\infty}^{\infty} dt\, \vec{d}_{\alpha\beta}\exp[-\tfrac{1}{2}\Gamma_\beta(t) + i(\Phi_{\alpha\beta} + \omega t)], \tag{11}$$

where $d^2B = B\,dB\,d\varphi_B$, Γ_β is the linewidth of state β, and $\Phi_{\alpha\beta}$ is the difference in phase between states α and β.

The dipole matrix elements $\vec{d}_{\alpha\beta}$ can be expressed in terms of those in the molecular coordinate system $(x'y'z')$ where the selection rules are operative. The molecular coordinates can be obtained by first rotating the space-fixed coordinate system with respect to the z axis through angle φ_B so that the xz plane coincides with the collision plane and then followed by a further rotation of the collision plane with respect to the y axis through angle γ so that the new z axis lies along the molecular axis $\hat{R}$. We

have

$$(d_{\alpha\beta})_x = \cos\varphi_B \cos\gamma (d_{\alpha\beta})_{x'} + \sin\varphi_B (d_{\alpha\beta})_{y'} - \cos\varphi_B \sin\gamma (d_{\alpha\beta})_{z'},$$
$$(d_{\alpha\beta})_y = -\sin\varphi_B \cos\gamma (d_{\alpha\beta})_{x'} + \cos\varphi_B (d_{\alpha\beta})_{y'} + \sin\varphi_B \sin\gamma (d_{\alpha\beta})_{z'}, \quad (12)$$
$$(d_{\alpha\beta})_z = \sin\gamma (d_{\alpha\beta})_{x'} + \cos\gamma (d_{\alpha\beta})_{z'}.$$

For transitions with $(d_{\alpha\beta})_{x'} = (d_{\alpha\beta})_{y'} = 0$ and $(d_{\alpha\beta})_{z'} \neq 0$, none of the three components of $\vec{d}_{\alpha\beta}$ is zero. In view that $\vec{q}\cdot\vec{B} = \kappa B \sin\theta_s \cos(\varphi_B - \varphi_s)$, where θ_s and φ_s are the polar and azimuthal angles of the scattered beam wave vector $\vec{\kappa}$, none of M_x, M_y, and M_z can in general be zero through the integration of φ_B in Eq. (11). If we integrate over the scattered beam direction $d\Omega = \sin\theta_s d\theta_s d\varphi_s$, the φ dependence of the spontaneous radiations drops out. The double differential cross section for spontaneous dipole radiations takes the (nonuniform) form

$$d^2\sigma_{\text{spon}}/d\omega\, d\Omega_{\vec{k}} \propto a + b\sin^2\theta, \quad \text{with} \quad a = 2\int d\Omega |M_x|^2, \quad b = \int d\Omega (|M_z|^2 - |M_x|^2). \quad (13)$$

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[1]F. W. Saris, W. F. van der Weg, H. Tawara, and R. Laubert, Phys. Rev. Lett. 28, 717 (1972).

[2]B. Müller and W. Greiner, Phys. Rev. Lett. 33, 469 (1974).

[3]See, for example, R. S. Thoe, I. A. Sellin, M. D. Brown, J. P. Forester, P. M. Griffin, D. J. Pegg, and R. S. Peterson, Phys. Rev. Lett. 34, 64 (1975), and references contained therein.

[4]See, for example, J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1962).

[5]J. C. Y. Chen, V. H. Ponce, and K. M. Watson, J. Phys. B: At. Mol. Phys. 6, 965 (1973); J. C. Y. Chen and K. M. Watson, Phys. Rev. 174, 152 (1968).

Hydrodynamics of ^{3}He near the A Transition

Mario Liu

Physik-Department der Technischen Universität, München, Germany

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The hydrodynamics of ^{3}He-A in the vicinity of the phase transition is generalized to include an extra variable, the magnitude of the order parameter. Its equation of motion is derived and added to the set of hydrodynamic equations. The effect on the dissipation and dispersion of first, second, and fourth sound is calculated. First sound is found to be anisotropic and a pair of new propagating modes is predicted.

Approaching the λ point of ^{4}He, ρ^s is determined by the local temperature and pressure only in the low-frequency limit.[1] The situation is quite analogous in ^{3}He, the only difference being the complexity of the order parameter $D_{\alpha i}$, which has eighteen real components. Five of them[2,3] correspond to different spontaneously broken symmetries; i.e., their spatial derivatives are equivalent to the superfluid velocity in ^{4}He. The rest become independent variables in the vicinity of the phase transition for all but the lowest frequencies. They do not obey conservation laws and relax with different characteristic times, all diverging with the same exponent as T approaches T_c. But, as will be shown below, only the magnitude of the order parameter, which is the exact counterpart of ρ^s, needs to be considered in the context of mass-transporting hydrodynamics. I shall denote the deviation of the magnitude from its equilibrium value, as defined in Eqs. (1), by Δ. With the inclusion of Δ as an additional thermodynamic variable and assuming the order-parameter symmetry of the axial state,[2,3] one can derive the equation of motion for Δ using standard procedures[4] of hydrodynamic theory for anisotropic systems.[5] With addition of this equation of motion to the set of hydrodynamic equations of ^{3}He-A,[6] first, second, and fourth sound have been recalculated. An additional pair of propagating modes due to the coupling of the fluctuation of Δ and the density arises in the high-frequency regime; their existence may be verified experimentally.

Out of nine complex components of $D_{\alpha i}$ only the three in the preferred spin direction may couple to hydrodynamic variables of ordinary space.