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Energy transfer from dark states: a relativistic approach

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Recently, a relativistic theory of energy transfer has been developed and shown to give rise to highly-important long-range phenomena for very large transferred energies where relativistic effects are crucial to include. Being general, the theory is also applicable for small and intermediate sized excess energies, where it describes retardation and magnetic effects. In this work we consider mainly energy transfer from dark states of the donor, *i.e.*, states which cannot decay radiatively by a dipole transition. Starting from the general full relativistic expressions for the various asymptotic contributions, we derive the leading terms describing the energy transfer for small and intermediate sized excess energies. It becomes evident that at small excess energies retardation and magnetic effects are essentially negligible compared to the impact of the bare Coulomb interaction. The situation can change drastically if one considers the transfer of intermediate sized energies as possible in the case of interatomic and intermolecular coulombic decay (ICD). Already a transfer of several hundreds of eV makes retardation effects similarly relevant as the Coulomb interaction at internuclear distances typical for equilibrium distances of weakly bound systems. Increasing the transferred energy further, the impact of retardation effects can overtake that of the bare Coulomb interaction between the donor and acceptor and even magnetic effects may become relevant. At such intermediate sized energies, a standard non-relativistic description of the participating donor and acceptor systems themselves is expected to suffice in computing the energy transfer, while the description of the energy transfer needs to take into account the relativistic effects as done here.

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I. Introduction

There is vast literature on energy-transfer processes. When an electronically excited molecule transfers its excess energy to a bound electronic state of its molecular neighbor, the process is known as Förster resonance energy transfer (FRET).[1] FRET has many applications, mainly in the condensed phase, *e.g.*, the first step of photosynthesis[2,3] and exciton transfer in semiconductors.[4] Owing to energy conservation, FRET is only possible if nuclear motion is involved, implying a timescale of picoseconds or longer.[2,3] Thus, FRET generally does not describe energy transfer between atoms. FRET is often treated within the QED formalism which provides additional insight and applications.[5,6]

Another, highly-efficient electronic-energy transfer process is interatomic and intermolecular coulombic decay (ICD)[7,8] operative between molecules as well as atoms. Here, an excited system transfers its excess energy to ionize a neighboring system, of course, provided that the excess energy is sufficiently high to ionize the neighbor. Being in the continuum, energy conservation is always fulfilled without the need for nuclear motion. Consequently, the excited system as well as the neighbor can be atoms or molecules and, importantly, the corresponding timescale of ICD is in the femtosecond regime even in the presence of a single neighbor.[8] Once the ICD channel is energetically open, the process takes place without the need for nuclear motion. However, to have a detailed comparison with experiment, the inclusion of nuclear motion can be of relevance. Calculations including the nuclear motion have been reported, see, *e.g.*, ref. 8 and references therein, and similar approaches can be also applied in the relativistic case. We stress that energy transfer processes typically become faster the more neighbors are present and, in the case of ICD, this has been computed and measured.[7–11] There are numerous applications of ICD varying from quantum halo systems with an extreme mean separation between the atoms,[12–14] quantum fluids[15] to quantum dots and wells.[16–18] Of general interest is that ICD is of potential relevance in radiation damage and for molecules of biological interest.[19–32]

In contrast to FRET, ICD can, in principle, take place for any amount of excess energy. Indeed, ICD has been measured and discussed, for example, after creating vacancies in the core of

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atoms.[33–35] To be able to describe ICD at much larger excess energies like those of deep core electrons of heavy elements, where neither the dipole approximation nor the Schrödinger equation apply, a relativistic theory of energy transfer has been recently developed.[36]

Apart from the fact that the newly developed theory describes ICD for very high transferred energies, the description incorporates retardation and magnetic effects even for the transfer of small energies. For such excess energies, energy transfer from bright states, *i.e.*, states which decay radiatively by a dipole transition, retardation effects have been derived by employing QED within the dipole approximation.[37] The contribution of these effects to the ICD rate is very interesting, but generally small. Of course, for small transferred energies, the relativistic theory reproduces the findings of the QED theory as explicitly shown in ref. 36. At large transferred energies, a relativistic approach is necessary, and the impact of the 'beyond Coulomb' terms has been shown to be very relevant.

In this work, we would like to investigate the impact of retardation as well as of magnetic effects on ICD from dark states, *i.e.*, states which do not decay radiatively *via* a dipole transition. We shall see that for small excess energies magnetic effects appear in the rates, in contrast to the situation for bright states. This is in accord with the QED derivation of FRET for dark states discussed for the condensed phase.[38] We shall see that for small energies the impact of retardation and magnetic effects on ICD is minor and we show that they can become substantial already for intermediate sized excess energies.

In the following section we will first briefly recapitulate the situation of the ICD rate for dark states when determined by employing the Coulomb interaction between the donor and acceptor. Then, we will investigate the impact of the relativistic Breit interaction which leads, as will be shown, to the appearance of retardation and magnetic effects. Finally, the range of relevance of these effects will be discussed.

II. Theoretical framework

A. Coulomb interaction and ICD

Consider a donor specified by D and an acceptor specified by A, where D and A can be atoms or molecules. The excited (or ionized excited) donor D* carries the excess energy $\hbar\omega = E_{D^*} - E_D$ which is transferred to A and ionizes it

$$D^* + A \rightarrow D + A^+ + e_{ICD}, \tag{1}$$

emitting the ICD electron e_{ICD}. As usual, the rate of the energy transfer process is given by

$$\Gamma_{ICD} = 2\pi |\langle I|V_C|F\rangle|^2, \tag{2}$$

where V_C is the Coulomb interaction between the electrons of the donor and those of the acceptor and $|I\rangle$ and $|F\rangle$ are the initial and final states of the process. Due to energy conservation, the total initial and final energies, E_I and E_F, fulfil $E_I = E_F$.

Now, there are two principal ways to evaluate the matrix element $\langle I|V_C|F\rangle$ which determines the ICD rate. The 'direct' way consists of considering the total donor–acceptor system as a single system and its states are computed using a suitable *ab initio* quantum mechanics method. Such methods and explicit calculations are available, see, *e.g.*, Green's functions[39–42] and coupled-cluster[43–46] approaches. In the second, 'explicit', way one assumes that the interatomic or intermolecular distance R between D and A is large and derives explicit analytical expressions for the matrix element. Such expressions provide much insight into the process at hand.

At large distances between D and A, the initial and final states $|I\rangle$ and $|F\rangle$ of the ICD process can each be expressed as a product of a donor and an acceptor state: $|I\rangle = |\Psi_{D^*}\rangle|\Phi_A\rangle$ and $|F\rangle = |\Psi_D\rangle|\Phi_{A^+}\rangle$. The meaning of the respective individual states is self explanatory. We only mention that, for brevity, $|\Phi_{A^+}\rangle$ is the state of the ionized acceptor including the emitted electron, taken to be energy normalized.

To continue, the Coulomb interaction between the electrons of D and A is expanded in inverse powers of R which, in the case of molecules, is the distance between the respective centers of mass of the nuclei. The coordinates of the donor's and acceptor's electrons are denoted by $\{\mathbf{x}_i\}$ and $\{\mathbf{x}'_j\}$, respectively. Now, new coordinates for the electrons of the donor relative to its center of mass at $\mathbf{R}_D$ and analogously for the acceptor, are introduced

$$\mathbf{r}_i = \mathbf{x}_i - \mathbf{R}_D, \tag{3}$$

$$\mathbf{r}'_j = \mathbf{x}'_j - \mathbf{R}_A. \tag{4}$$

Then, the distance between an electron of the donor and an electron of the acceptor reads

$$|\mathbf{x}_i - \mathbf{x}'_j| = R\left|\mathbf{u}_{DA} + \frac{\mathbf{r}_i - \mathbf{r}'_j}{R}\right|. \tag{5}$$

Here and in the following, $\mathbf{u}_{DA} = \dfrac{\mathbf{R}_D - \mathbf{R}_A}{R}$ is the unit vector pointing from the center of mass of the donor to that of the acceptor. This all enables a straightforward expansion of the distance between the electrons:

$$\begin{aligned} |\mathbf{x}_i - \mathbf{x}'_j| &= R\left[1 + \left(\frac{\beta}{R}\right)\right]^{\frac{1}{2}} \\ &= R\left[1 + \frac{1}{2}\left(\frac{\beta}{R}\right) - \frac{1}{8}\left(\frac{\beta}{R}\right)^2 + \frac{3}{48}\left(\frac{\beta}{R}\right)^3 + \ldots\right] \\ \beta &= 2\mathbf{u}_{DA}\cdot\left(\mathbf{r}_i - \mathbf{r}'_j\right) + \frac{\left(\mathbf{r}_i - \mathbf{r}'_j\right)^2}{R}. \end{aligned} \tag{6}$$

With the above, the expansion of the Coulomb interaction and later on of the Breit interaction can be calculated.

The expansion of the Coulomb interaction up to $1/R^4$ reads

$$\begin{aligned} V_C &= \sum_{i,j}\frac{1}{|\mathbf{x}_i - \mathbf{x}'_j|} \\ &= \frac{\hat{\mathbf{d}}^D\cdot\hat{\mathbf{d}}^A - 3\left(\mathbf{u}_{DA}\cdot\hat{\mathbf{d}}^D\right)\left(\mathbf{u}_{DA}\cdot\hat{\mathbf{d}}^A\right)}{R^3} + \frac{9\hat{q}^D_{\parallel}\hat{d}^A_{\parallel} - 6\hat{\mathbf{q}}^D_{\perp}\cdot\hat{\mathbf{d}}^A_{\perp}}{2R^4}, \end{aligned} \tag{7}$$

where only the terms which contribute to the transition matrix element $\langle \mathrm{I}|V_\mathrm{C}|\mathrm{F}\rangle$, *i.e.*, which are products of donor and acceptor terms, are listed. Here,

$$\begin{aligned}\hat{\mathbf{d}}^\mathrm{D} &= \sum_\mathrm{i} \mathbf{r}_\mathrm{i} \\ \mathbf{d}^\mathrm{D} &= \sum_\mathrm{i} \langle \Psi_{\mathrm{D}^*}|\mathbf{r}_\mathrm{i}|\Psi_\mathrm{D}\rangle = \left\langle \Psi_{\mathrm{D}^*}\middle|\hat{\mathbf{d}}^\mathrm{D}\middle|\Psi_\mathrm{D}\right\rangle\end{aligned} \tag{8}$$

is the electronic dipole moment operator of the donor and the resulting transition dipole moment. These quantities are defined analogously for the acceptor.

The quantities $\hat{q}^\mathrm{D}_\parallel$ and $\hat{q}^\mathrm{D}_\perp$ appearing above relate to the traceless quadrupole moment operator of the donor which deserves further attention. This operator is a traceless tensor and the subscripts $\parallel$ and $\perp$ refer to components parallel or perpendicular to the unit vector $\mathbf{u}_\mathrm{DA}$. Explicitly,

$$\begin{aligned}\hat{q}^\mathrm{D}_\parallel &= \sum_\mathrm{i}\left[(\mathbf{u}_\mathrm{DA}\cdot\mathbf{r}_\mathrm{i})^2 - \mathbf{r}_\mathrm{i}^2/3\right] \\ q^\mathrm{D}_\parallel &= \left\langle \Psi_{\mathrm{D}^*}\middle|\hat{q}^\mathrm{D}_\parallel\middle|\Psi_\mathrm{D}\right\rangle,\end{aligned} \tag{9}$$

and

$$\begin{aligned}\hat{q}^\mathrm{D}_\perp\cdot\hat{d}^\mathrm{A}_\perp &= \sum_{\mathrm{i,j}}(\mathbf{u}_\mathrm{DA}\cdot\mathbf{r}_\mathrm{i})\left[(\mathbf{r}_\mathrm{i}\cdot\mathbf{r}'_\mathrm{j}) - (\mathbf{u}_\mathrm{DA}\cdot\mathbf{r}_\mathrm{i})(\mathbf{u}_\mathrm{DA}\cdot\mathbf{r}'_\mathrm{j})\right] \\ q^\mathrm{D}_\perp\cdot d^\mathrm{A}_\perp &= \langle \Psi_{\mathrm{D}^*}|\hat{\mathbf{q}}^\mathrm{D}_\perp|\Psi_\mathrm{D}\rangle\cdot\left\langle \Psi_\mathrm{A}\middle|\hat{\mathbf{d}}^\mathrm{A}_\perp\middle|\Psi_{\mathrm{A}^+}\right\rangle.\end{aligned} \tag{10}$$

With eqn (7) and the notations (8)–(10), one readily finds

$$\begin{aligned}\langle \mathrm{I}|V_\mathrm{C}|\mathrm{F}\rangle = &\frac{\mathbf{d}^\mathrm{D}\cdot\mathbf{d}^\mathrm{A} - 3\left(\mathbf{u}_\mathrm{DA}\cdot\mathbf{d}^\mathrm{D}\right)\left(\mathbf{u}_\mathrm{DA}\cdot\mathbf{d}^\mathrm{A}\right)}{R^3} \\ &+\frac{9q^\mathrm{D}_\parallel d^\mathrm{A}_\parallel - 6q^\mathrm{D}_\perp\cdot d^\mathrm{A}_\perp}{2R^4},\end{aligned} \tag{11}$$

for the matrix element determining the energy transfer rate. The term $\propto 1/R^3$ describes the transition due to dipole–dipole and the term $\propto 1/R^4$ quadrupole–dipole donor–acceptor interaction. The next term would be $\propto 1/R^5$ and is due to quadrupole–quadrupole interactions.

For energy transfer from a bright state, the leading term dominates and the ICD rate (after averaging over the random orientation of the donor and acceptor) reads:[47]

$$\Gamma_\mathrm{ICD} = \frac{3\hbar}{4\pi}\left(\frac{c}{\omega}\right)^4\frac{\gamma^\mathrm{D}\sigma^\mathrm{A}}{R^6}, \tag{12}$$

where γ^D is the radiative rate (Einstein coefficient) of the isolated donor and σ^A is the photoionization cross section of the acceptor at a photon energy of $\hbar\omega$. The above expression allows for an estimate of the ICD rate using experimentally determined data. Importantly, the true power of ICD lies in finding that its rate can be orders of magnitude larger than that predicted by the above formula at intermolecular distances as in weakly bound systems like clusters and liquids.[47]

For energy transfer from a dark state, the transition dipole moment $\mathbf{d}^\mathrm{D}$ of the donor vanishes and we are left with the quadrupole–dipole term $\propto 1/R^4$ in eqn (11). The respective ICD rate now takes on the following appearance:[47]

$$\Gamma_\mathrm{ICD} = \frac{1323\hbar}{28\pi}\left(\frac{c}{\omega}\right)^6\frac{\gamma^\mathrm{D}\sigma^A}{R^8}, \tag{13}$$

where the radiative rate γ^D now relates to the quadrupole transition of the donor.

To make contact with the notation of the quadrupole moment elements in ref. 47, we define the direction of the unit vector $\mathbf{u}_\mathrm{DA}$, connecting the centers of mass of the donor and acceptor, as the z-axis of our coordinate system. Then, it is easy to see from eqn (9) and (10) that $q^\mathrm{D}_\parallel = q^\mathrm{D}_{zz}$ and $q^\mathrm{D}_\perp\cdot d^\mathrm{A}_\perp = q^\mathrm{D}_{xz}d^\mathrm{A}_x + q^\mathrm{D}_{yz}d^\mathrm{A}_y$. Note that in ref. 47, Q is used and not q.

Since this work is on energy transfer from dark states, we briefly address the example presented in ref. 47 before turning to the discussion of retardation and magnetic effects for dark states. Ionization of the 3d subshell of Zn leads to the possible vacancies $3d_0$, $3d_{\pm1}$ and $3d_{\pm2}$. In Zn, these vacancies can only be filled by the transition from a 4s electron orbital. This transition is dipole forbidden and ICD can take place for the $3d_0$ and $3d_{\pm1}$ vacancies *via* quadrupole–dipole and for the $3d_{\pm2}$ vacancy *via* quadrupole–quadrupole, transitions. Fig. 1 shows the results of the asymptotic expression eqn (13) and the respective one $\propto 1/R^{10}$ not discussed here for the $3d_{\pm2}$ vacancy for ICD in the BaZn dimer. These results are compared with the those of *ab initio* computations.

As seen in the figure, at equilibrium geometry, the *ab initio* determined rate is about three orders of magnitude larger than that predicted by the asymptotic expression. According to the *ab initio* prediction, the ICD lifetime is in the fs regime while the asymptotic expression predicts this lifetime to be in the ps

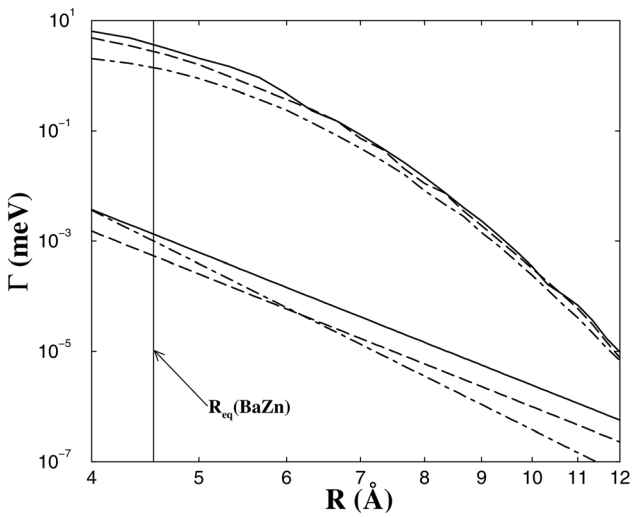

Fig. 1 Total ICD rates of BaZn resulting from Zn 3d sub-shell ionization as a function of the internuclear distance R. The vertical line indicates the equilibrium distance R_eq of the BaZn dimer. The three upper curves show the *ab initio* calculated results for Γ_0, $\Gamma_{\pm1}$, and $\Gamma_{\pm2}$. The three lower curves show the quadrupole–dipole (Γ_0, $\Gamma_{\pm1}$) and the quadrupole–quadrupole ($\Gamma_{\pm2}$) asymptotic approximations resulting from the Coulomb interaction (see text). Solid lines: $3d_0$ vacancy; dashed lines: $3d_{\pm1}$ vacancy; dash–dot lines: $3d_{\pm2}$ vacancy. Reproduced with permission from the American Physical Society, ref. 47, Copyright 2004.

regime. It is only for distances $R > 12$ Å that the asymptotic approximation becomes accurate. The value of the asymptotic expression can be better appreciated if one realizes that the radiative lifetime of the 3d vacancy of an isolated Zn atom is just about 2 μs,[48] *i.e.*, the asymptotic expression predicts the ICD lifetime to be shorter than the radiative lifetime by about 6 orders of magnitude. Finally, we note that the Auger (also called Auger–Meitner) decay of the 3d hole is energetically closed.

B. Breit interaction and ICD

As discussed above, using the Coulomb interaction, the usual asymptotic expression for the ICD rate of bright states exhibits a behavior proportional to $1/R^6$. By employing QED within the dipole approximation, it has been demonstrated that retardation leads to additional, longer range, terms $\propto 1/R^4$ and $\propto 1/R^2$.[37] For energy transfer from dark states, the ICD rate shows a behavior proportional to $1/R^8$ (we concentrate on quadrupole–dipole transitions). Our relativistic approach reproduced in the dipole approximation the findings of QED for bright states.[36] The appearance of longer range terms found for bright states motivated us to investigate their possible appearance for dark states.

In general, relativistic effects can shift and split levels computed by the non-relativistic Schrödinger equation and, thus, energetically closed ICD channels in the non-relativistic case may become ICD active.[49] Using the Dirac equation to compute the asymptotic ICD rate, one obtains a rate proportional to $1/R^6$ as in the non-relativistic case because of the Coulomb interaction contained in the Dirac equation.[50,51] In other words, the Dirac equation has to be augmented by the Breit interaction[52] in order to include retardation and magnetic effects.

The single-electron Dirac Hamiltonian for electron i reads

$$h(i) = c\boldsymbol{\alpha}_i\cdot\mathbf{p}_i + (\beta_i - 1)m_e c^2 + W(\mathbf{r}_i), \tag{14}$$

where c is the velocity of light, $\mathbf{p}_i$ is the vector of the momenta and $\boldsymbol{\alpha}_i$ is the vector of the 4-dimensional Dirac matrices. The potential $W(\mathbf{r}_i)$ is the Coulomb interaction of the electron with the nuclei. The electronic coordinate $\mathbf{r}_i$ is with respect to the nuclear center of mass.

The many-electron Dirac–Breit Hamiltonian at fixed nuclear coordinates takes on the appearance:[52,53]

$$H = \sum_i h(i) + \sum_{i>j} g(i,j) + W_0. \tag{15}$$

Here, $g(i, j)$ is the electron–electron interaction containing the Breit interaction (see below) and W_0 is the Coulomb repulsion of the nuclei.

As already mentioned above, one has to include the frequency dependent Breit interaction in order to take into account retardation and magnetic effects. This interaction, determined by QED theory, is caused by the exchange of a virtual photon between the interacting electrons.[52,53] The form of the Breit interaction depends on the gauge used for the propagator for photons.[54] There are two popular forms widely employed, one which follows from the Feynman (Lorenz) gauge and one by choosing the Coulomb gauge, and we mention that they do not necessarily lead to identical results.[55,56] Both gauges have been used in ref. 36. Here, we concentrate on the Feynman (Lorenz) gauge.

The electron–electron interaction $\sum_{i,j} g(i,j)$ between those of the donor and those of the acceptor deserves particular attention. We shall call this interaction V_ω in the following. To proceed, we have to take care that the coordinates of their electrons have a common coordinate system. The Breit interaction in the Feynman gauge reads:

$$V_\omega^{\mathrm{F}} = \sum_{i,j} \frac{1 - \boldsymbol{\alpha}_i\cdot\boldsymbol{\alpha}'_j}{|\mathbf{x}_i - \mathbf{x}'_j|}\, e^{i\frac{\omega}{c}|\mathbf{x}_i - \mathbf{x}'_j|}. \tag{16}$$

Note that in the Feynman gauge, the Coulomb potential does not appear explicitly as an additive term of the Breit interaction.

Analogous to eqn (2), the ICD rate now reads

$$\Gamma_{\mathrm{ICD}} = 2\pi|\langle \mathrm{I}|V_\omega|\mathrm{F}\rangle|^2. \tag{17}$$

The general expansion of V_ω and of $\langle \mathrm{I}|V_\omega|\mathrm{F}\rangle$ in inverse powers of R up to the third power has been discussed.[36]

In the following section, we discuss the expansion of the matrix element $\langle \mathrm{I}|V_\omega|\mathrm{F}\rangle$ which determines the ICD rate for small and intermediate sized excess energies up to the term $\propto 1/R^4$ relevant for energy transfer from dark states.

C. Expansion in powers of $1/R$: small energies

1. Energy transfer from bright states. Let us start with energy transfer from a bright state. At small energies $\hbar\omega$, the dipole approximation is valid. If we collect for each term $\propto 1/R^n$ the leading contribution in ω/c, we find[36]

$$\langle \mathrm{I}|V_\omega|\mathrm{F}\rangle = e^{i\frac{\omega}{c}R}\left[\left(\frac{\omega}{c}\right)^2\frac{-S^{\mathrm{DA}} + S_\parallel^{\mathrm{DA}}}{R} + i\left(\frac{\omega}{c}\right)\frac{-S^{\mathrm{DA}} + 3S_\parallel^{\mathrm{DA}}}{R^2} + \frac{S^{\mathrm{DA}} - 3S_\parallel^{\mathrm{DA}}}{R^3}\right],$$
$$S^{\mathrm{DA}} = \mathbf{d}^{\mathrm{D}}\cdot\mathbf{d}^{\mathrm{A}},\quad S_\parallel^{\mathrm{DA}} = \left(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{d}^{\mathrm{D}}\right)\left(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{d}^{\mathrm{A}}\right). \tag{18}$$

The appearance of this matrix element is identical to the result obtained using QED and the dipole approximation.[37] See also ref. 57, where the result of ref. 37 is given in the present notation. As seen, the expression of the term $\propto 1/R^3$ is identical to that obtained using the bare Coulomb interaction in eqn (11), except for the phase factor $e^{i\frac{\omega}{c}R}$. This factor does not contribute to the ICD rate though. However, there is a subtle difference between the QED and Coulomb results on the one hand and the result in eqn (18) on the other hand. The latter has been derived for relativistic states which are solutions of the Dirac–Breit Hamiltonian, and the former for states which are solutions of the Schrödinger equation. For small energies, the differences are expected to be minor, but they might be of some importance for intermediate sized energies like core energies of light atoms where $\omega a_0/c < 1$ (a_0 is the Bohr radius). Of course, for $\omega a_0/c > 1$ eqn (18) is meaningless as it has been

derived for small energies. Then, the full relativistic results discussed in ref. 36 have to be considered.

2. Energy transfer from dark states at very large R. Next, we turn to energy transfer from dark states. As the transition dipole moments vanish, all terms in eqn (18) also vanish and we have to compute the next leading contributions in powers of $(\omega/c)^n$ as well as extend the discussion to the term $\propto 1/R^4$, as we have already seen in Section II A. for the bare Coulomb case.

For large excess energies, when the donor is embedded in an environment containing many acceptors, the long range contribution $\propto 1/R$ is the most relevant.[36] We shall see below that even for small energies this contribution is particularly interesting. We start with the full relativistic compact expression:[36]

$$\langle \mathrm{I}|V_\omega|\mathrm{F}\rangle = \frac{\mathrm{e}^{i\frac{\omega}{c}R}}{R}\left[\epsilon^{\mathrm{D}}\epsilon^{\mathrm{A}} - \boldsymbol{\epsilon}_{\boldsymbol{\alpha}}^{\mathrm{D}}\cdot\boldsymbol{\epsilon}_{\boldsymbol{\alpha}}^{\mathrm{A}}\right], \tag{19}$$

where we have used the following abbreviations

$$\begin{aligned}
\epsilon^{\mathrm{D}} &= \sum_{\mathrm{i}}\left\langle \Psi_{\mathrm{D}^*}\middle|\mathrm{e}^{i\frac{\omega}{c}(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{r}_{\mathrm{i}})}\middle|\Psi_{\mathrm{D}}\right\rangle,\\
\epsilon^{\mathrm{A}} &= \sum_{\mathrm{j}}\left\langle \Psi_{\mathrm{A}}\middle|\mathrm{e}^{-i\frac{\omega}{c}(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{r}'_{\mathrm{j}})}\middle|\Psi_{\mathrm{A}^+}\right\rangle,\\
\boldsymbol{\epsilon}_{\boldsymbol{\alpha}}^{\mathrm{D}} &= \sum_{\mathrm{i}}\left\langle \Psi_{\mathrm{D}^*}\middle|\mathrm{e}^{i\frac{\omega}{c}(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{r}_{\mathrm{i}})}\boldsymbol{\alpha}_{\mathrm{i}}\middle|\Psi_{\mathrm{D}}\right\rangle,\\
\boldsymbol{\epsilon}_{\boldsymbol{\alpha}}^{\mathrm{A}} &= \sum_{\mathrm{j}}\left\langle \Psi_{\mathrm{A}}\middle|\boldsymbol{\alpha}_{\mathrm{j}}\mathrm{e}^{-i\frac{\omega}{c}(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{r}'_{\mathrm{j}})}\middle|\Psi_{\mathrm{A}^+}\right\rangle.
\end{aligned} \tag{20}$$

Let us first evaluate $\epsilon^{\mathrm{D}}\epsilon^{\mathrm{A}}$. The leading term in power of (ω/c) is obtained by expanding the phase factor $\mathrm{e}^{i\frac{\omega}{c}(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{r}_{\mathrm{i}})}$ in ϵ^{D} up to second order and the respective factor in ϵ^{A} up to first order. One obtains $\epsilon^{\mathrm{D}}\epsilon^{\mathrm{A}} = \frac{i}{2}\left(\frac{\omega}{c}\right)^3\langle\Psi_{\mathrm{D}^*}|\sum_{\mathrm{i}}(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{r}_{\mathrm{i}})^2|\Psi_{\mathrm{D}}\rangle d_\parallel^{\mathrm{A}}$. It is much more involved to evaluate the second term in eqn (19). For finding the leading term in power of (ω/c) it suffices to expand the phase factor in $\boldsymbol{\epsilon}_{\boldsymbol{\alpha}}^{\mathrm{D}}$ up to first order and to zeroth order in $\boldsymbol{\epsilon}_{\boldsymbol{\alpha}}^{\mathrm{A}}$ as every Dirac matrix introduces a quantity energy/c, see below. It is helpful to first introduce the following relation between coordinates and Dirac matrices, see, *e.g.*, ref. 58

$$\boldsymbol{\alpha}_{\mathrm{i}} = \frac{i}{\hbar c}[H,\mathbf{r}_{\mathrm{i}}], \tag{21}$$

which immediately gives $\boldsymbol{\epsilon}_{\boldsymbol{\alpha}}^{\mathrm{A}} = -i\left(\frac{\omega}{c}\right)\mathbf{d}^{\mathrm{A}}$. The evaluation of $\boldsymbol{\epsilon}_{\boldsymbol{\alpha}}^{\mathrm{D}}$ is more complicated. Since the transition $\mathrm{D}^*\rightarrow\mathrm{D}$ is optically forbidden, one has as the leading term in power of (ω/c)

$$\begin{aligned}
\epsilon_{\boldsymbol{\alpha}}^{\mathrm{D}} &= i\frac{\omega}{c}\sum_{\mathrm{i}}\langle\Psi_{\mathrm{D}^*}|(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{r}_{\mathrm{i}})\boldsymbol{\alpha}_{\mathrm{i}}|\Psi_{\mathrm{D}}\rangle\\
&= \frac{i\,\omega}{2\,c}\left[\sum_{\mathrm{i}}\langle\Psi_{\mathrm{D}^*}|(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{r}_{\mathrm{i}})\boldsymbol{\alpha}_{\mathrm{i}}|\Psi_{\mathrm{D}}\rangle + \sum_{\mathrm{i}}\langle\Psi_{\mathrm{D}^*}|\boldsymbol{\alpha}_{\mathrm{i}}(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{r}_{\mathrm{i}})|\Psi_{\mathrm{D}}\rangle\right].
\end{aligned} \tag{22}$$

Here, the Dirac matrices cannot be replaced by coordinates alone. However, inserting the relation in eqn (21) into the above equation, we arrive at the useful identity:

$$\begin{aligned}
&\langle\Psi_{\mathrm{D}^*}|(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{r}_{\mathrm{i}})\boldsymbol{\alpha}_{\mathrm{i}}|\Psi_{\mathrm{D}}\rangle\\
&= \left\langle\Psi_{\mathrm{D}^*}\middle|\left\{\frac{i\omega}{2c}(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{r}_{\mathrm{i}})\mathbf{r}_{\mathrm{i}} + \frac{1}{2}[(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{r}_{\mathrm{i}})\boldsymbol{\alpha}_{\mathrm{i}} - (\mathbf{u}_{\mathrm{DA}}\cdot\boldsymbol{\alpha}_{\mathrm{i}})\mathbf{r}_{\mathrm{i}}]\right\}\middle|\Psi_{\mathrm{D}}\right\rangle,\\
&\langle\Psi_{\mathrm{A}}|(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{r}'_{\mathrm{j}})\boldsymbol{\alpha}'_{\mathrm{j}}|\Psi_{\mathrm{A}^+}\rangle\\
&= \left\langle\Psi_{\mathrm{A}}\middle|\left\{-\frac{i\omega}{2c}(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{r}'_{\mathrm{j}})\mathbf{r}'_{\mathrm{j}} + \frac{1}{2}[(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{r}'_{\mathrm{j}})\boldsymbol{\alpha}'_{\mathrm{j}} - (\mathbf{u}_{\mathrm{DA}}\cdot\boldsymbol{\alpha}'_{\mathrm{j}})\mathbf{r}'_{\mathrm{j}}]\right\}\middle|\Psi_{\mathrm{A}^+}\right\rangle,
\end{aligned} \tag{23}$$

where we have also given the respective identity for the acceptor in case one is interested in the situation that A cannot be ionized by a dipole transition.

One sees that there are two basic contributions to the matrix element $\langle\mathrm{I}|V_\omega|\mathrm{F}\rangle$ which determines the ICD rate at large distances. The first can be expressed by electronic coordinates and will be identified below with quadrupole transition moments, while the Dirac matrices cannot be eliminated from the second contribution. It is illuminating to analyze the latter contribution in detail.

We introduce the appealing vectors and their respective transition matrix element

$$\begin{aligned}
\boldsymbol{\mathcal{L}} &= \sum_{\mathrm{i}}\boldsymbol{\mathcal{L}}_{\mathrm{i}} = \sum_{\mathrm{i}}\mathbf{r}_{\mathrm{i}}\times\boldsymbol{\alpha}_{\mathrm{i}} = (\mathcal{L}_x,\mathcal{L}_y,\mathcal{L}_z)\\
\boldsymbol{\mathcal{L}}^{\mathrm{D}} &= \langle\Psi_{\mathrm{D}^*}|\boldsymbol{\mathcal{L}}|\Psi_{\mathrm{D}}\rangle.
\end{aligned} \tag{24}$$

We call $\boldsymbol{\mathcal{L}}$ the relativistic angular moment. Choosing the z-axis to be parallel to the unit vector $\mathbf{u}_{\mathrm{DA}}$, one readily finds

$$\sum_{\mathrm{i}}[(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{r}_{\mathrm{i}})\boldsymbol{\alpha}_{\mathrm{i}} - (\mathbf{u}_{\mathrm{DA}}\cdot\boldsymbol{\alpha}_{\mathrm{i}})\mathbf{r}_{\mathrm{i}}] = (\mathcal{L}_y,-\mathcal{L}_x,0). \tag{25}$$

As this term contributes to $\langle\mathrm{I}|V_\omega|\mathrm{F}\rangle$ *via* the scalar product $\boldsymbol{\epsilon}_{\boldsymbol{\alpha}}^{\mathrm{D}}\cdot\boldsymbol{\epsilon}_{\boldsymbol{\alpha}}^{\mathrm{A}}$, see eqn (19), the quantity $\mathcal{L}_x^{\mathrm{D}}d_y^{\mathrm{A}} - \mathcal{L}_y^{\mathrm{D}}d_x^{\mathrm{A}}$ arises which is nothing but the z-component of the cross product $\boldsymbol{\mathcal{L}}^{\mathrm{D}}\times\mathbf{d}^{\mathrm{A}}$. In an arbitrary coordinate system, this component is the one parallel to $\mathbf{u}_{\mathrm{DA}}$ and is specified as $\left(\boldsymbol{\mathcal{L}}^{\mathrm{D}}\times\mathbf{d}^{\mathrm{A}}\right)_\parallel$.

We are now in the position to collect all contributions and express them by dipole, quadrupole and relativistic angular moments. The final result takes on the compact appearance

$$\langle I|V_\omega|F\rangle = -\frac{\mathrm{e}^{i\frac{\omega}{c}R}}{R}\left[\frac{i}{2}\left(\frac{\omega}{c}\right)^3\mathbf{q}_\perp^{\mathrm{D}}\cdot\mathbf{d}_\perp^{\mathrm{A}} + \frac{1}{2}\left(\frac{\omega}{c}\right)^2\left(\boldsymbol{\mathcal{L}}^{\mathrm{D}}\times\mathbf{d}^{\mathrm{A}}\right)_\parallel\right], \tag{26}$$

where the scalar product $\mathbf{q}_\perp^{\mathrm{D}}\cdot\mathbf{d}_\perp^{\mathrm{A}}$ has been introduced and discussed in Section II A. Comparing with the result (11) for the bare Coulomb interaction, we see that apart from the different power of $1/R$, the parallel component of the quadrupole moment $q_\parallel^{\mathrm{D}}$ does not appear in eqn (26), but instead a magnetic term appears. As typical, electric quadrupole and magnetic dipole transitions appear together in relativistic theory.[59,60]

3. Energy transfer from dark states: the remaining terms. As found in eqn (26), the leading contribution in powers of $(\omega/c)^n$ to the central matrix element $\langle\mathrm{I}|V_\omega|\mathrm{F}\rangle$ is of third power (we note that a Dirac matrix scales as energy/c, see eqn (21)).

Analogously, the leading contribution to the term $\langle \mathrm{I}|V_\omega|\mathrm{F}\rangle$ proportional to $1/R^2$ scales as $(\omega/c)^2$, that proportional to $1/R^3$ scales as $(\omega/c)^1$ and finally the scaling is $(\omega/c)^0$ for the term proportional to $1/R^4$. The situation is a reminder of the finding in eqn (18) for energy transfer from bright states.

To proceed, we make use of the complete list of the explicit expressions contributing to the terms of $\langle \mathrm{I}|V_\omega|\mathrm{F}\rangle$ proportional to $1/R^2$ and $1/R^3$ which are provided in Appendix B in ref. 36. There, the expressions are ordered in growing powers of (ω/c) which is helpful in collecting the leading contributions to the matrix element. As done in the preceding Section II C2, the phase factor is expanded in a Taylor series to the needed term and then use is made of eqn (21).

In the case of $\langle \mathrm{I}|V_\omega|\mathrm{F}\rangle \propto 1/R^2$, the quantity $\boldsymbol{\epsilon}_\alpha^{\mathrm{D}}$ appears, see eqn (22), and is evaluated as in eqn (23)–(25). Collecting all contributions and expressing them as above by dipole, quadrupole and relativistic angular moments, one obtains:

$$\frac{e^{i\frac{\omega}{c}R}}{R^2}\left\{\frac{3}{2}\left(\frac{\omega}{c}\right)^2\left[\mathbf{q}_\perp^{\mathrm{D}}\cdot\mathbf{d}_\perp^{\mathrm{A}}-q_\parallel^{\mathrm{D}}d_\parallel^{\mathrm{A}}+\frac{2}{3}q_0^{\mathrm{D}}d_\parallel^{\mathrm{A}}\right]+\frac{i}{2}\left(\frac{\omega}{c}\right)\left(\boldsymbol{\mathcal{L}}^{\mathrm{D}}\times\mathbf{d}^{\mathrm{A}}\right)_\parallel\right\}. \tag{27}$$

Here, in contrast to the term $\propto 1/R$ in eqn (26), the parallel component of the quadrupole moment appears and, in contrast to all terms, see below, also the isotropic quadrupole moment $q_0^{\mathrm{D}}=\left\langle \Psi_{\mathrm{D}^*}\middle|\sum_i r_i^2\middle|\Psi_{\mathrm{D}}\right\rangle$.

The evaluation of the leading contributions to the terms $\propto 1/R^3$ and, in particular, $\propto 1/R^4$, is less involved since the relativistic angular moment does not appear. Because the leading contributions to the term $\propto 1/R^4$ scale as $(\omega/c)^0$, the result is, up to the phase factor $e^{i\frac{\omega}{c}R}$ identical to eqn (11) for the bare Coulomb interaction. The final result for these terms reads

$$e^{i\frac{\omega}{c}R}\left[9q_\parallel^{\mathrm{D}}d_\parallel^{\mathrm{A}}-6\mathbf{q}_\perp^{\mathrm{D}}\cdot\mathbf{d}_\perp^{\mathrm{A}}\right]\frac{1}{2}\left[\left(-\frac{i\omega}{c}\right)\frac{1}{R^3}+\frac{1}{R^4}\right]. \tag{28}$$

Note that except for the factor $\pm i\omega/c$, the coefficient of the term $\propto 1/R^3$ is the same as that of the term $\propto 1/R^4$, and the same applies for the terms $\propto 1/R^2$ and $\propto 1/R^3$ describing energy transfer from bright states, see eqn (18).

D. Expansion in powers of $1/R$: intermediate energies

1. Energy transfer from bright states: corrections. In Section II C., we have derived the leading contribution in powers of ω/c of each of the $1/R$-Taylor expansion terms of the transfer matrix element $\langle \mathrm{I}|V_\omega|\mathrm{F}\rangle$ determining the energy transfer rate. Obviously, the results obtained are valid for small transferred energies. What about intermediate sized energies, where $\omega a_0/c$ (a_0 = 1 a.u.) is still well smaller than 1 allowing for collecting the next leading contributions in powers of ω/c? Notice that as c = 137 a.u., ω/c = 1 implies a rather large excess energy of 3781 eV which is above the binding energy of the K 1s core electron. In other words, there is a large range of energies available, where $\omega/c \ll 1$.

We can take advantage of the fact that the starting point has been the full relativistic expression of the $1/R$-Taylor expansion determined in ref. 36 and, in principle, determine as many contributions in powers of ω/c as one wishes. An additional advantage of such an approach is that all appearing relevant quantities, like energies and multipole moments, are expressed with the Dirac–Breit relativistic wavefunctions of the donor and acceptor.

For energy transfer from bright states there is no need for further derivation. One just has to add the leading contributions given in eqn (18) and those in eqn (26)–(28). The latter constitute the next order corrections to the former. For completeness, we express the collected terms explicitly in a compact form:

$$\langle \mathrm{I}|V_\omega|\mathrm{F}\rangle = e^{i\frac{\omega}{c}R}\sum_{n=1}^{4}\left[\frac{\left(\frac{\omega}{c}\right)^{3-n}M_n+\left(\frac{\omega}{c}\right)^{4-n}C_n}{R^n}\right], \tag{29}$$

where the following abbreviations are used for the 'main' quantities M_n

$$\begin{aligned} M_1 &= -\mathbf{d}^{\mathrm{D}}\cdot\mathbf{d}^{\mathrm{A}}+\left(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{d}^{\mathrm{D}}\right)\left(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{d}^{\mathrm{A}}\right),\\ M_2 &= -iM_3 = i\left[-\mathbf{d}^{\mathrm{D}}\cdot\mathbf{d}^{\mathrm{A}}+3\left(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{d}^{\mathrm{D}}\right)\left(\mathbf{u}_{\mathrm{DA}}\cdot\mathbf{d}^{\mathrm{A}}\right)\right],\\ M_4 &= 0, \end{aligned} \tag{30}$$

and for the 'corrections' C_n

$$\begin{aligned} C_1 &= -\frac{i}{2}\mathbf{q}_\perp^{\mathrm{D}}\cdot\mathbf{d}_\perp^{\mathrm{A}}-\frac{1}{2}\left(\frac{c}{\omega}\right)\left(\boldsymbol{\mathcal{L}}^{\mathrm{D}}\times\mathbf{d}^{\mathrm{A}}\right)_\parallel,\\ C_2 &= \frac{3}{2}\left[\mathbf{q}_\perp^{\mathrm{D}}\cdot\mathbf{d}_\perp^{\mathrm{A}}-q_\parallel^{\mathrm{D}}d_\parallel^{\mathrm{A}}+\frac{2}{3}q_0^{\mathrm{D}}d_\parallel^{\mathrm{A}}\right]+\frac{i}{2}\left(\frac{c}{\omega}\right)\left(\boldsymbol{\mathcal{L}}^{\mathrm{D}}\times\mathbf{d}^{\mathrm{A}}\right)_\parallel,\\ C_3 &= -iC_4 = \frac{i}{2}\left[6\mathbf{q}_\perp^{\mathrm{D}}\cdot\mathbf{d}_\perp^{\mathrm{A}}-9q_\parallel^{\mathrm{D}}d_\parallel^{\mathrm{A}}\right]. \end{aligned} \tag{31}$$

Note that the relativistic angular moment, see eqn (24), contains a Dirac matrix which scales as energy/c.

2. Energy transfer from dark states: discussion. In complete analogy to the spirit of the preceding section, one can use the explicit terms provided in ref. 36 for the expansion of the energy transfer matrix element to obtain the next leading contributions in powers of ω/c also for dark states. As many terms appear containing various sextupole and octupole moments and, in addition, as we expect these moments to be rather small in general, we refrain from listing them. Instead, we will discuss the relevance of the terms derived in this work.

Let us return to the weakly bound BaZn dimer discussed in Section II A. To remove an electron from Zn 4s requires 9.39 eV and from Zn 3d, 17.51 eV.[61] After ionizing the Zn 3d shell a 4s electron fills this vacancy and the excess energy available is 8.12 eV (= 0.29 a.u.) sufficient to undergo ICD with the Ba neighbor. The ICD rate in eqn (13) stems from the term of the matrix element $\propto 1/R^4$, see eqn (11) and (28). As discussed above, this rate is much larger than the radiative rate of the isolated Zn 3d vacancy, explaining the dominance of ICD, but still much smaller than the *ab initio* result, see Fig. 1. As can be seen in eqn (26)–(28), the terms due to retardation and magnetic effects provide a less steep decline with R of the matrix element and hence of the ICD rate. Each power of $1/R$ less than

$1/R^4$ is accompanied by a factor ω/c. For Zn, $\omega/c = 2 \times 10^{-3}$ which implies that R should be about 2.5×10^2 Å in order to contribute similarly as the term $\propto 1/R^4$. At such long distances the overall ICD rate is rather small, see Fig. 1.

Having seen that for BaZn the impact of retardation and magnetic effects on ICD after Zn 3d ionization is small compared to the impact of the bare Coulomb interaction, we ask at what scenarios do we expect these effects to be relevant. We mention two scenarios.

The remarks made in the preceding section, suggest that choosing systems and transitions with substantially larger excess energies is advantageous. For simplicity, we first consider ions with a Zn-like core. Ionizing the 3d shell of Xe^{24+}, for instance, provides excess energies from the 4s → 3d transitions of 582 eV ($3d_{5/2}$) and 595 eV ($3d_{3/2}$).[62] These lead to $\omega/c \approx 0.15$. Following the above discussion, the term $\propto 1/R^3$ will contribute similarly to the term $\propto 1/R^4$ already at about the equilibrium distance of the BaZn dimer, see eqn (28). The excess energy available after removing an electron from the 3d shell of Au^{49+} is estimated to be about 1500 eV[63] and thus $\omega/c \approx 0.39$, implying that the two terms $\propto 1/R^3$ and $\propto 1/R^4$ contribute the same already at a distance of about 1.35 Å. Of course, the impact of retardation falls off slower with distance than that of the bare Coulomb interaction. In other words, taking into account all the terms contributing to the ICD, collected in eqn (26)–(28), one can expect the retardation and magnetic effects to be the dominating ones in the energy transfer from the above dark states.

Highly charged ions are often used as projectiles in experiments and, more recently, also for investigating ICD, see ref. 32 and 64. In these cases, ICD is induced by the collision, but not by energy transfer from the ion as discussed in this work. It might, therefore, be more suitable from a practical point of view, to investigate ICD starting from a neutral heavy atom and a neighbor, like in the example of the BaZn dimer. We may use again Xe and Au as above, but as neutral atoms. The conclusion drawn above, that retardation and magnetic effects dominate the contribution to ICD by the bare Coulomb interaction for essentially all values of R, applies also to the case of ionizing the 3d shell of these neutral atoms. However, the situation differs in that the created 3d vacancy in the ions discussed above is a dark state, while in the neutrals there are many channels for ICD since there are many electrons energetically above the vacancy. In that sense, one can characterize the transitions filling the vacancy and leading to ICD with a neighbor as either bright or dark transitions. As each transition gives rise to an ICD electron emitted from the neighbor with a characteristic kinetic energy, one can, in principle, discriminate the channels.

As a last point of this first scenario, we would like to mention that the radiative rates due to quadrupole transitions can be expected to be larger for the same kind of vacancies in the heavier elements[65] and this may enhance the respective ICD rate. Of course, much depends on the suitability of the neighboring system, in particular, on its photoionization cross section at the respective energy corresponding to the excess energy.

In the second scenario we consider a donor embedded in an extended environment containing many acceptors. The situation has been discussed in detail in ref. 36 and we only briefly address it here in connection with energy transfer *via* a dark transition. Employing the full Dirac–Breit theory and assuming the various donors to interact weakly with each other and, for simplicity, to be homogeneously spherically distributed around the donor, gives rise to the following simple expression for the total ICD rate:

$$\Gamma_{\mathrm{ICD}}^{\mathrm{total}} = \Gamma_{\mathrm{ICD}}^{\mathrm{total}}(0, R_0) + \gamma^{\mathrm{D}} \mathrm{e}^{-R_0/R_{\mathrm{att}}}. \quad (32)$$

Here, $\Gamma_{\mathrm{ICD}}^{\mathrm{total}}(0, R_0)$ is the ICD rate due to the neighboring acceptors within a distance R_0 from the donor chosen to be large enough such that the matrix element in eqn (26) applies for $R \gtrapprox R_0$. As we have seen in Fig. 1, this rate can be rather larger than predicted by asymptotic expansions. Consequently, it is advisable to compute this quantity by other means, *e.g.*, by relativistic *ab initio* methods, if possible. Furthermore, this quantity grows substantially with the number of neighbors.[8–11] R_{att} is the attenuation length parameter describing the losses a photon beam has in matter.[66–68] This parameter depends on the photon energy and is typically larger for larger energies.

As seen from eqn (32), the remote acceptors alone can suppress the radiation of the donor, provided that $R_{\mathrm{att}} \gg R_0$, which is expected to be the case for larger excess energies. Interestingly, the radiative rate γ^{D} of the donor grows with the photon energy the donor would emit if isolated,[65] and, nevertheless, this radiation will be suppressed.

III. Conclusion

By employing the Dirac–Breit Hamiltonian, where the Dirac Hamiltonian has been complemented by the frequency dependent Breit interaction, we are able to derive and analyze asymptotic expressions for energy transfer incorporating relativistic effects. Here, we expand the general full relativistic expressions derived recently to obtain the various asymptotic contributions in the leading powers of ω/c ($\hbar\omega$ is the energy transferred). The work first concentrates on energy transfer from dark states of the donor, *i.e.*, states which cannot decay radiatively by a dipole transition. Except of the derivations themselves, the main goal is to analyze the terms arising due to retardation and magnetic effects and to assess whether they can be of relevance for energy transfer from dark states.

From the expressions obtained it becomes evident that retardation and magnetic effects are essentially negligible for energy transfer between a dark bound electronic state of the donor and a bound state of the acceptor compared to the impact of the bare Coulomb interaction. This applies as well to the case of ICD at small energies as the detailed discussion of the BaZn dimer after Zn 3d ionization demonstrates.

However, it becomes clear that the situation can change drastically if one considers the transfer of intermediate sized energies as possible in the case of ICD. Already a transfer of about 500 eV energy makes retardation effects similarly

relevant as the Coulomb interaction at internuclear distances typical for equilibrium distances of weakly bound dimers. Obviously, when increasing the transferred energy further, the impact of retardation effects can overtake that of the bare Coulomb interaction between the donor and acceptor and even magnetic effects may become relevant. At such intermediate sized energies, standard non-relativistic calculations should suffice to obtain reliable transition quadrupole moments and energies. At substantially higher energies, one will have to resort to relativistic calculations, and as the quotient $\omega a_0/c$ is no longer a small quantity, the expansion employed here cannot be used, and the full relativistic expressions derived recently have to be considered.

Dark states with intermediate sized excess energies are available, for instance, in highly charged atomic ions. Such atoms are used in experiments, also on ICD. A particularly transparent situation is found for ions isoelectronic with neutral Zn. But, in principle, one is not confined to dark states in order to apply the present approach. To arrive at sufficiently large excess energies in neutral atoms, dark transitions of many-electron atoms can be envisaged. For instance, after removing a 3d electron of Xe, there are many channels available for ICD with a neighbor, some of them are from the transition of an s electron to fill the 3d vacancy. Measuring the kinetic energy of the ICD electron allows one to identify the dark transition in question. In this context we mention that not only the excess energies, but also the absolute values of the quadrupole moments, are expected to typically grow for the same kind of vacancies in the heavier elements and this too may enhance the respective ICD rate.

As found for energy transfer from bright states of the donor, the true power of ICD becomes apparent also for transfer from dark states, by employing *ab initio* methods to compute the ICD rate. At equilibrium geometry of weakly bound systems, the *ab initio* computed rates can be orders of magnitude larger than those computed by the asymptotic expressions. This might be even more so for transfer from dark states because the presence of a close-by neighbor can reduce the symmetry of the donor enhancing the ICD. Nevertheless, the asymptotic expressions are very useful in understanding and estimating whether a given constellation is relevant to ICD, see also Section II A. Of course, the asymptotic expressions become reliable estimates at larger distances between the donor and acceptor. Retardation and magnetic effects become particularly relevant at very large distances in the presence of many donors. Here, the full Dirac–Breit theory predicts a paradigm, namely that much of the radiative rate is suppressed and turned into ICD.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data that supports the findings of this study are available from the corresponding author upon reasonable request.

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References

1 T. Förster, *Ann. Phys.*, 1948, **437**, 55.
2 T. Renger, V. May and O. Kühn, *Phys. Rep.*, 2001, **343**, 137.
3 G. D. Scholes, G. R. Fleming, A. Olaya-Castro and R. van Grondelle, *Nat. Chem.*, 2011, **3**, 763.
4 V. Stehr, R. F. Fink, M. Tafipolski, C. Deibel and B. Engels, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2016, **6**, 694.
5 G. A. Jones and D. S. Bradshaw, *Front. Phys.*, 2019, **7**, 100.
6 R. D. Jenkins and D. L. Andrews, *J. Phys. Chem. A*, 1998, **102**, 10834.
7 L. S. Cederbaum, J. Zobeley and F. Tarantelli, *Phys. Rev. Lett.*, 1997, **79**, 4778.
8 T. Jahnke, U. Hergenhahn, B. Winter, R. Dörner, U. Früling, P. V. Demekhin, K. Gokherg, L. S. Cederbaum, A. Ehresmann and A. Knie, *et al.*, *Chem. Rev.*, 2020, **120**, 11295.
9 G. Öhrwall, M. Tchaplyguine, M. Lundwall, R. Feifel, H. Bergersen, T. Rander, A. Lindblad, A. Schulz, S. Peredkov and S. Barth, *et al.*, *Phys. Rev. Lett.*, 2004, **93**, 173401.
10 E. Fasshauer, *New J. Phys.*, 2016, **18**, 043028.
11 C. Küstner-Wetekam, L. Marder, D. BloÃŸ, C. Honisch, N. Kiefer, C. Richter, S. Rubik, S. Rebecca Schaf, C. Zindel and M. Förstel, *et al.*, *Commun. Phys.*, 2023, **6**, 50.
12 N. Sisourat, N. V. Kryzhevoi, P. Kolorenc, S. Scheit, T. Jahnke and L. S. Cederbaum, *Nat. Phys.*, 2010, **6**, 508–511.
13 T. Havermeier, T. Jahnke, K. Kreidi, R. Wallauer, S. Voss, M. Schöffler, S. Schössler, L. Foucar, N. Neumann and J. Titze, *et al.*, *Phys. Rev. Lett.*, 2010, **104**, 133401.
14 A. Ben-Asher, A. Landau, L. S. Cederbaum and N. Moiseyev, *J. Phys. Chem. Lett.*, 2020, **11**, 6600.
15 A. C. LaForge, L. Ben Ltaief, S. R. Krishnan, N. Sisourat and M. Mudrich, *Rep. Prog. Phys.*, 2024, **87**, 126402.
16 T. Goldzak, L. Gantz, I. Gilary, G. Bahir and N. Moiseyev, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2015, **91**, 165312.
17 A. Bande, K. Gokhberg and L. S. Cederbaum, *J. Chem. Phys.*, 2011, **135**, 144112.
18 I. Cherkes and N. Moiseyev, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **83**, 113303.
19 R. W. Howell, *Int. J. Radiat. Biol.*, 2008, **84**, 959–975.
20 T. Jahnke, H. Sann, T. Havermeier, K. Kreidi, C. Stuck, M. Meckel, M. Schöffler, N. Neumann, R. Wallauer and S. Voss, *et al.*, *Nat. Phys.*, 2010, **6**, 139.
21 M. Mucke, M. Braune, S. Barth, M. Förstel, T. Lischke, V. Ulrich, T. Arion, U. Becker, A. Bradshaw and U. Hergenhahn, *Nat. Phys.*, 2010, **6**, 143.
22 P. Zhang, C. Perry, T. T. Luu, D. Matselyukh and H. J. Wörner, *Phys. Rev. Lett.*, 2022, **128**, 133001.
23 S. D. Stoychev, A. I. Kuleff and L. S. Cederbaum, *J. Am. Chem. Soc.*, 2011, **133**, 6817.
24 U. Hergenhahn, *Int. J. Radiat. Biol.*, 2012, **88**, 871.

25 K. Gokhberg, P. Kolorenc, A. I. Kuleff and L. S. Cederbaum, *Nature*, 2014, **505**, 661.
26 F. Trinter, M. S. Schöffler, H.-K. Kim, F. P. Sturm, K. Cole, N. Neumann, A. Vredenborg, J. Williams, I. Bocharova and R. Guillemin, *et al.*, *Nature*, 2014, **505**, 664.
27 S. Xu, D. Guo, X. Ma, X. Zhu, W. Feng, S. Yan, D. Zhao, Y. Gao, S. Zhang and X. Ren, *et al.*, *Angew. Chem., Int. Ed.*, 2018, **57**, 17023.
28 V. Stumpf, K. Gokhberg and L. S. Cederbaum, *Nat. Chem.*, 2016, **8**, 237.
29 G. Gopakumar, I. Unger, P. Slavícek, U. Hergenhahn, G. Öhrwall, S. Malerz, D. Céolin, F. Trinter, B. Winter and I. Wilkinson, *et al.*, *Nat. Chem.*, 2023, **15**, 1408.
30 D. BloÃŸ, F. Trinter, I. Unger, C. Zindel, C. Honisch, J. Viehmann, N. Kiefer, L. Marder, C. Küstner-Wetekam and E. Heikura, *et al.*, *Nat. Commun.*, 2024, **15**, 4594.
31 S. Barik, S. Dutta, N. R. Behera, R. K. Kushawaha, Y. Sajeev and G. Aravind, *Nat. Chem.*, 2022, **14**, 1098.
32 Y. Gao, A. D. Skitnevskaya, E. Wang, H. Yuan, X. Ren, H. Lin, Z. Yan, S. Zhang, S. Gu and B. Yang, *et al.*, *Phys. Rev. X*, 2025, **15**, 011053.
33 G. Öhrwall, N. Ottosson, W. Pokapanich, S. Legendre, S. Svensson and O. Björneholm, *J. Phys. Chem. B*, 2010, **114**, 17057.
34 A. Hans, C. Kuestner-Wetekam, P. Schmidt, C. Ozga, X. Holzapfel, H. Otto, C. Zindel, C. Richter, L. S. Cederbaum and A. Ehresmann, *et al.*, *Phys. Rev. Res.*, 2020, **2**, 012022(R).
35 A. Hans, P. Schmidt, C. Küstner-Wetekam, F. Trinter, S. Deinert, D. BloÃŸ, J. H. Viehmann, R. Schaf, M. Gerstel and C. M. Saak, *et al.*, *J. Phys. Chem. Lett.*, 2021, **12**, 7146.
36 L. S. Cederbaum and J. Hofierka, *J. Chem. Phys.*, 2025, **162**, 124109.
37 J. Hemmerich, R. Bennett and S. Buhmann, *Nat. Commun.*, 2018, **9**, 2934.
38 G. D. Scholes and D. L. Andrews, *J. Chem. Phys.*, 1997, **107**, 5374.
39 J. Zobeley, L. S. Cederbaum and F. Tarantelli, *J. Phys. Chem. A*, 1999, **103**, 11145.
40 V. Averbukh and L. S. Cederbaum, *J. Chem. Phys.*, 2005, **123**, 204107.
41 P. Kolorenc and V. Averbukh, *J. Chem. Phys.*, 2020, **152**, 214107.
42 N. Vaval and L. S. Cederbaum, *J. Chem. Phys.*, 2007, **126**, 164110.
43 R. Kumar, A. Ghosh and N. Vaval, *J. Chem. Theor. Comput.*, 2022, **18**, 807.
44 A. Ghosh, S. Pal and N. Vaval, *J. Chem. Phys.*, 2013, **139**, 064112.
45 N. K. Jayadev, W. Skomorowski and A. I. Krylov, *J. Phys. Chem. Lett.*, 2023, **14**, 8612.
46 V. Parravicini and T.-C. Jagau, *J. Chem. Phys.*, 2023, **159**, 094112.
47 V. Averbukh, I. B. Müller and L. S. Cederbaum, *Phys. Rev. Lett.*, 2004, **93**, 263002.
48 L. D. Schearer and W. C. Holton, *Phys. Rev. Lett.*, 1970, **24**, 1214.
49 M. Pernpointner, N. V. Kryzhevoi and S. Urbaczek, *J. Chem. Phys.*, 2008, **129**, 024304.
50 E. Fasshauer, K. Gokhberg and M. Pernpointner, *J. Chem. Phys.*, 2013, **138**, 014305.
51 M. Förstel, M. Mucke, T. Arion, T. Lischke, M. Pernpointner, U. Hergenhahn and E. Fasshauer, *J. Phys. Chem. C*, 2016, **120**, 22957.
52 I. P. Grant, *Relativistic Quantum Theory of Atoms and Molecules*, Springer, New York, 2006, ISBN 978-0387346717.
53 M. Reiher and A. Wolf, *Relativistic Quantum Chemistry*, Wiley, Weinheim, 2009, ISBN 978-3527312924.
54 I. P. G. H. M. Quiney and S. Wilson, *On the Relativistic Many-Body Perturbation Theory of Atomic and Molecular Electronic Structure*, Springer, Berlin, 1989, ISBN 978-3540510277.
55 J. Sucher, *J. Phys. B: At., Mol. Opt. Phys.*, 1988, **21**, L585.
56 E. Lindroth and A. M. Masrtensson-Pendrill, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1989, **39**, 3794.
57 J. Hofierka and L. S. Cederbaum, *Phys. Rev. A*, 2024, **109**, 052812.
58 N. H. List, T. R. L. Melin, M. van Horn and T. Saue, *J. Chem. Phys.*, 2020, **152**, 184110.
59 G. H. Shortley, *Phys. Rev.*, 1940, **57**, 225.
60 C. M. Dodson and R. Zia, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **86**, 125102.
61 A. Kramida, Y. Ralchenko, J. Reader and NIST-ASD-Team, *NIST atomic spectra database*, National Institute of Standards and Technology, Gaithersburg, MD, 2019.
62 P. Liu, J. Zeng, A. Borovik, S. Schippers and A. Müller, *Phys. Rev. A: At., Mol., Opt. Phys.*, 2015, **92**, 012701.
63 J. A. Bearden and A. F. Burr, *Rev. Mod. Phys.*, 1967, **39**, 125.
64 J. Schwestka, A. Niggas, S. Creutzburg, R. Kozubek, R. Heller, M. Schleberger, R. A. Wilhelm and F. Aumayr, *J. Phys. Chem. Lett.*, 2019, **10**, 4805.
65 U. I. Safronova, A. S. Safronova and P. Beiersdorfer, *J. Phys. B: At., Mol. Opt. Phys.*, 2006, **39**, 4491.
66 W. Heitler, *The Quantum Theory of Radiation*, Courier Corporation, 1984.
67 C. T. Chantler, *J. Phys. Chem. Ref. Data*, 1995, **24**, 71.
68 M. Berger, J. Hubbell, S. Seltzer, J. Coursey and D. Zucker, *XCOM: Photon Cross Section Database (version 1.2)*, 1999.

