THE JOURNAL OF PHYSICAL CHEMISTRY A

Article

pubs.acs.org/JPCA

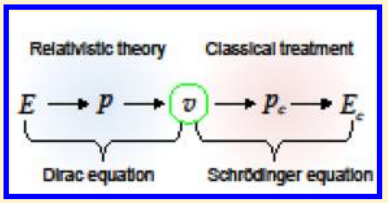
Relativistic Effects in Photon-Induced Near Field Electron Microscopy

Sang Tae Park and Ahmed H. Zewail*

Physical Biology Center for Ultrafast Science and Technology, Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, United States

Supporting Information

ABSTRACT: Electrons and photons, when interacting via a nanostructure, produce a new way of imaging in space and time, termed photon-induced near field electron microscopy or PINEM [Barwick et al. *Nature* **2009**, *462*, 902]. The phenomenon was described by considering the evanescent field produced by the nanostructure, but quantification of the experimental results was achieved by solving the Schrödinger equation for the interaction of the three bodies. The question remained, is the nonrelativistic formulation sufficient for this description? Here, relativistic and nonrelativistic quantum mechanical formulations are compared for electron−photon interaction mediated by nanostructures, and it is shown that there is an exact equivalence for the two formulations. The nonrelativistic formulation was found to be valid in the relativistic regime when using in the former formulation the relativistically corrected velocity (and the corresponding values of momentum and energy). In the PINEM experiment, 200 keV electrons were utilized, giving the experimental (relativistically corrected) velocity to be 0.7c (v without relativistic correction is 0.885c). When this value (0.7c), together with those of the corresponding momentum ($p_c = mv$) and energy ($E_c = (1/2)mv^2$), is used in the first order solution of the Schrödinger formulation, an exact equivalence is obtained.



INTRODUCTION

The Dirac equation[1,2] successfully unifies quantum mechanics with special relativity, and in so doing the existence of electron spin[3] and antimatter[4] was predicted and verified. For dynamics, a fundamental concept of localization in quantum mechanics is the wave packet. Extensive studies of the nature of wave packet and the Dirac equation have been made.[5−10] Of particular interest is the wave packet propagation under electromagnetic interaction,[11−16] especially in the relativistic regime of motion.

In a recent publication from this group,[17] the interaction between electrons and photons, mediated by a nanostructure, was studied using a nonrelativistic quantum mechanics formulation to describe the phenomenon observed in photon-induced near-field electron microscopy, PINEM.[18,19] The nonrelativistic formulation is in excellent accordance with a weak-interaction limit,[20] a seminumerical quantum scattering theory,[21] and a continuous beam case.[22] The theoretical findings describe the experimental results quite well. But it may be argued that the nonrelativistic formulation is inapplicable in this PINEM regime, because the electron kinetic energy of interest was 200 keV, which gives $v/c = 0.7$ and $\gamma = 1.4$, a value that is fairly relativistic.

In the nonrelativistic approach,[17] the classical momentum and energy were used and corresponded to the observed (relativistic) electron velocity. In this way, the momentum and the energy changes correspond to those of the photon used, and the dispersion relation of the electron, $\partial E/\partial p = v$, is satisfied. In the relativistic regime, however, the expression may require a correction by a relativistic factor or using a relativistic mass.

In this paper, the nonrelativistic formulation is extended to account for the high velocities used in PINEM. The equivalence of the two is established even when the electrons used experimentally have a velocity that reaches the speed of light.

THEORY

Nonrelativistic Formulation. A detailed derivation of transition probability of PINEM in the nonrelativistic formulation is given in a previous publication,[17] where the time-dependent Schrödinger equation of a free electron in the presence of scattered electromagnetic waves was analytically solved to a first order. Here, we briefly summarize the result. (See Appendix A in ref 17 for notations and detailed derivations.) The wave function of the electron is defined in terms of the envelope function, $f(z, t)$, such that $\Psi(z, t) = f(z, t) \exp[i(k_c z - \omega_c t)]$, where k_c and ω_c are chosen to correspond to the actual (relativistic) velocity, v_0, such that $\hbar k_c = mv_0$ and $\hbar\omega_c = (1/2)mv_0^2$. The envelope function carries the initial wave packet profile and the final phase change due to the interaction with the scattered electric field. Using the Coulomb gauge, such that $\nabla\cdot\vec{A} = 0$, the time-dependent one-dimensional Schrödinger equation then becomes

$$\frac{\partial f}{\partial t} + \frac{\hbar k_c}{m}\frac{\partial f}{\partial z} - \frac{i\hbar}{2m}\frac{\partial^2 f}{\partial z^2} = +i\frac{k_c q}{m}A_z f + \frac{q}{m}A_z\frac{\partial f}{\partial z} + \frac{q^2 A_z^2}{2i\hbar m}f \quad (1)$$

where $q = -e$ is the electron charge, m is the electron mass, and A_z is the z-component of the vector potential, $\vec{A}$. The second and the third terms on the left-hand side are the propagation and the dispersion terms, respectively. For our time scale, the dispersion term can be ignored. For the high kinetic energy electron (200 keV) used, the second term on the right-hand side can also

Special Issue: Jörn Manz Festschrift

Received: May 9, 2012
Revised: June 26, 2012
Published: June 28, 2012

   dx.doi.org/10.1021/jp304534n | *J. Phys. Chem. A* 2012, 116, 11128−11133

be ignored as $|k_c f| \gg |(1/i)(\partial f/\partial z)|$. Finally, the third term on the right-hand side (ponderomotive term) is ignored for the same reason (for relatively weak radiation), and we obtain:

$$\frac{\partial f(z)}{\partial t} + \frac{\hbar k_c}{m}\frac{\partial f(z)}{\partial z} \approx +i\frac{k_c q}{m}A_z(z, t)\, f(z) \tag{2}$$

It is convenient to redefine the envelope function on the moving frame, $g(z',t')$, such that $f(z,t) = g(z - v_0 t, t)$. The moving frame, $z' = z - v_0 t$, is chosen to be at the same velocity as the group velocity of the electron packet, using $\hbar k_c/m = v_0$. Then the propagation term is canceled and eq 2 reduces to

$$\frac{\partial g(z')}{\partial t} \approx +i\frac{q v_0}{\hbar}A_z(z' + v_0 t, t)\, g(z') \tag{3}$$

which is an ordinary differential equation with the solution given by

$$g(z', t) = g(z', t_0)\exp\left[i\frac{q v_0}{\hbar}\int_{t_0}^{t} \mathrm{d}t'\, A_z(z' + v_0 t', t')\right] \tag{4}$$

Here, we only consider the electric field of the (scattered) photon. When we define the field integral,

$$\tilde{F}\left(\frac{\omega_p}{v_0}\right) \equiv \int_{-\infty}^{+\infty} \mathrm{d}z''\, \tilde{E}_z(z'', 0)\exp\left[-i\frac{\omega_p}{v_0}z''\right] \tag{5}$$

which is the Fourier transform component of the scattered electric field at $\Delta k = \omega_p/v_0$, the final envelope function becomes (see Appendix A in ref 17 for detail):

$$\frac{g(z', +\infty)}{g(z', -\infty)} = \exp\left[i\frac{q}{\hbar\omega_p}\,\mathrm{Im}\left\{\exp\left[i\frac{\omega_p}{v_0}z'\right]\tilde{F}\right\}\exp\left[-\frac{(z' + v_0\tau)^2}{4{v_0}^2{\sigma_p}^2}\right]\right] \tag{6}$$

Equation 6 can be transformed to a discrete summation (Jacobi-Anger relation[23]), giving

$$\frac{g(z', +\infty)}{g(z', -\infty)} = \sum_{n=-\infty}^{+\infty}\exp\left[in\frac{\omega_p}{v_0}z'\right]\left(-\frac{\tilde{F}}{|\tilde{F}|}\right)^n J_n\left(\frac{-q}{\hbar\omega_p}|\tilde{F}|\exp\left[-\frac{(z' + v_0\tau)^2}{4{v_0}^2{\sigma_p}^2}\right]\right) \tag{7}$$

where J_n is the Bessel function of the first kind. The final state wave function is retrieved from $\Psi(z,t) = g(z - v_0 t, t)\exp[i(k_c z - \omega_c t)]$ at $t \to +\infty$, which becomes

$$\Psi(z, t) = \sum_{n=-\infty}^{+\infty} g_n(z - v_0 t)\exp[i(k_n z - \omega_n t)] \tag{8}$$

where $k_n = k_c + n(\omega_p/v_0)$, $\omega_n = \omega_c + n\omega_p$, $g_n(z') = g(z', -\infty)\,\xi_n(z')$, and

$$\xi_n(z') = \left(-\frac{\tilde{F}}{|\tilde{F}|}\right)^n J_n\left(\frac{-q}{\hbar\omega_p}|\tilde{F}|\exp\left[-\frac{(z' + v_0\tau)^2}{4v_0^2\sigma_p^2}\right]\right)$$

the wave function in momentum space becomes

$$\Psi(k) = \sum_{n=-\infty}^{+\infty}\mathcal{F}\{g_n;\, k - k_n\} \tag{9}$$

and the probability for each wavelet becomes

$$P_n \approx \int_{-\infty}^{+\infty}\mathrm{d}k\, |\mathcal{F}\{g_n;\, k - k_n\}|^2 = \int_{-\infty}^{+\infty}\mathrm{d}z'\, |g_n(z')|^2 \tag{10}$$

Relativistic Formulation. Now, we derive the relativistic formulation of PINEM. It is beneficial to recall the relativistic relations of

$$\gamma = \frac{1}{\sqrt{1 - \left(\frac{v}{c}\right)^2}} = \sqrt{1 + \left(\frac{p}{mc}\right)^2} = \frac{E}{mc^2} \tag{11}$$

where γ is the relativistic factor, m is the mass at rest, c is the speed of light, v is the velocity, p is the momentum, and E is the relativistic energy, such that the kinetic energy is given by $T = E - mc^2$.

The Dirac equation for an electron in an electromagnetic wave is given by

$$i\hbar\frac{\partial\Psi}{\partial t} = \{c\boldsymbol{\alpha}\cdot(\vec{p} - q\vec{A}) + q\phi + \boldsymbol{\beta}mc^2\}\Psi \tag{12}$$

where $q = -e$ is the electron charge, $\vec{A}$ is the vector potential, and ϕ is the scalar potential. $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are unit constant matrices chosen to satisfy the relativistic energy-momentum relation. Similar to the previous nonrelativistic treatment,[17] we only consider a one-dimensional wave function, since the momentum change in the transverse direction is negligible compared to that in the longitudinal direction. For a one-dimensional equation, along the z-direction, $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$, and Ψ are given by two components (see Supporting Information).

In the absence of the electromagnetic wave, the continuous planar wave solution of momentum, p, is given as,

$$\Psi^+ = \begin{pmatrix} u_1^+ \\ u_2^+ \end{pmatrix}\exp[i(kz - \omega^+ t)] \tag{13}$$

$$\Psi^- = \begin{pmatrix} u_1^- \\ u_2^- \end{pmatrix}\exp[i(kz - \omega^- t)] \tag{14}$$

where

$$\hbar k = p$$

$$\hbar\omega^+ = E^+ = +\sqrt{p^2c^2 + m^2c^4}$$

$$\hbar\omega^- = E^- = -\sqrt{p^2c^2 + m^2c^4}$$

$$u_1^+ = \frac{E^+ + mc^2}{\sqrt{2E^+(E^+ + mc^2)}} = \sqrt{\frac{\gamma + 1}{2\gamma}}$$

$$u_2^+ = \frac{pc}{\sqrt{2E^+(E^+ + mc^2)}} = \pm\sqrt{\frac{\gamma - 1}{2\gamma}}$$

$$u_1^- = -\frac{pc}{\sqrt{2E^-(E^- - mc^2)}} = \mp\sqrt{\frac{\gamma - 1}{2\gamma}}$$

$$u_2^- = -\frac{E^- - mc^2}{\sqrt{2E^-(E^- - mc^2)}} = \sqrt{\frac{\gamma + 1}{2\gamma}}$$

dx.doi.org/10.1021/jp304534n | J. Phys. Chem. A 2012, 116, 11128−11133

The positive energy solution corresponds to the matter, electron, and the negative energy solution corresponds to the antimatter, positron.

A Gaussian wave packet for the Dirac equation can also be constructed by superposition of a spectrum of positive-energy planar wave solutions,

$$\Psi(k) = \sqrt{\hat{G}(k - k_0; \sigma_k)} \begin{pmatrix} u_1^+(k) \\ u_2^+(k) \end{pmatrix} \tag{15}$$

where $\hat{G}$ is a Gaussian momentum profile (see Supporting Information) and k_0 corresponds to the mean value of momentum. However, both the profile and the coefficients, u_1^+ and u_2^+, depend on the magnitude of the momentum (see Figure 1). For a fairly narrow spectrum of

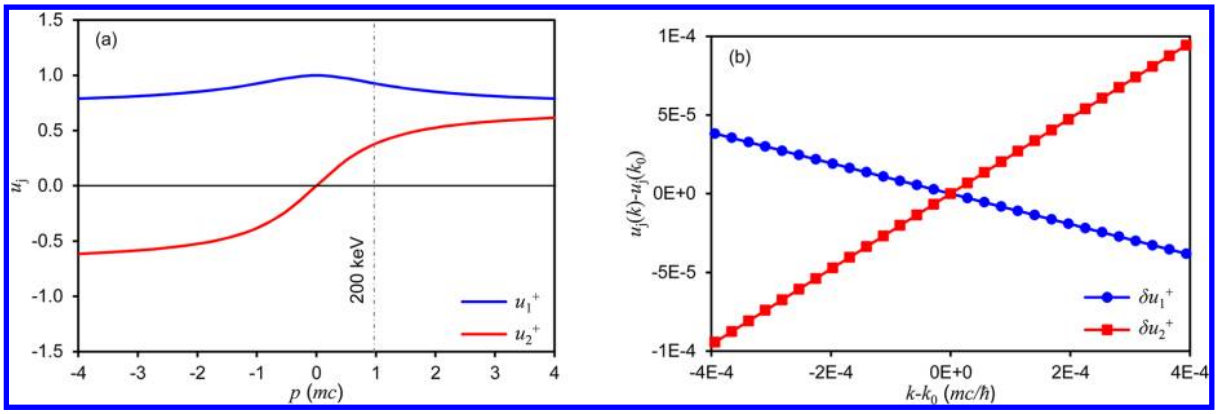


Figure 1. (a) Absolute and (b) relative dependences of Dirac spinor coefficients on the momentum. Symbols in (b) correspond to 10 eV intervals from 200 keV which is shown as a vertical dashed line in (a).

momentum, coefficients can be linearly approximated as $u_j^+(k) \approx u_j^+(k_0) + (k - k_0)(\mathrm{d}u_j^+/\mathrm{d}k)|_{k=k_0}$. Under this linear approximation, using the properties of Fourier transformation with respect to translation and differentiation (see Supporting Information), and $\sigma_z = 1/(2\sigma_k)$, we obtain

$$\Psi(z) \approx \sqrt{G(z; \sigma_z)} \begin{pmatrix} u_1^+(k_0) \\ u_2^+(k_0) \end{pmatrix} e^{ik_0 z} - i \frac{\mathrm{d}\sqrt{G(z; \sigma_z)}}{\mathrm{d}z} \begin{pmatrix} \frac{\mathrm{d}u_1^+}{\mathrm{d}k} \\ \frac{\mathrm{d}u_2^+}{\mathrm{d}k} \end{pmatrix}_{k=k_0} e^{ik_0 z} \tag{16}$$

where

$$\frac{du_1^+}{dk} = -\frac{1}{2\gamma^2}\sqrt{\frac{\gamma - 1}{2\gamma}}\left(\frac{\hbar}{mc}\right) = \frac{\lambda\!\!\!^{-}_C}{2\gamma^2} u_1^-$$

$$\frac{du_2^+}{dk} = +\frac{1}{2\gamma^2}\sqrt{\frac{\gamma + 1}{2\gamma}}\left(\frac{\hbar}{mc}\right) = \frac{\lambda\!\!\!^{-}_C}{2\gamma^2} u_2^-$$

and $\lambda\!\!\!^{-}_C = \hbar/mc$ is the reduced Compton wavelength. When represented in a spatial wave packet, it contains a small imaginary contribution, which becomes an antimatter-like component. It will be shown later that this antimatter-like component is in fact a part of an electron wave packet. It is convenient to define the envelope functions, f^+ and f^-, with the positive and the negative energy components as

$$\Psi(z, t) = f^+(z, t) \begin{pmatrix} u_1^+(k_0) \\ u_2^+(k_0) \end{pmatrix} \exp[i(k_0 z - \omega_0^+ t)] + f^-(z, t) \begin{pmatrix} u_1^-(k_0) \\ u_2^-(k_0) \end{pmatrix} \exp[i(k_0 z - \omega_0^- t)] \tag{17}$$

dx.doi.org/10.1021/jp304534n | J. Phys. Chem. A 2012, 116, 11128−11133

The evolution of the wave packet is then described by $f^+(z,t)$ and $f^-(z,t)$, which can be solved using eq 12. By substituting eq 17 in eq 12 with nonzero vector potential and eliminating quantities that satisfy energy−momentum relations of planar wave solutions, we obtain the Dirac equation in terms of the envelope functions,

$$\frac{\partial f^+}{c\partial t} + \frac{\sqrt{\gamma_0^2 - 1}}{\gamma_0}\frac{\partial f^+}{\partial z} + \frac{1}{\gamma_0}\frac{\partial f^-}{\partial z}\exp[i(\omega_0^+ - \omega_0^-)t] = i\frac{q}{\hbar}A_z\left(+\frac{\sqrt{\gamma_0^2 - 1}}{\gamma_0}f^+ + \frac{1}{\gamma_0}f^-\exp[i(\omega_0^+ - \omega_0^-)t]\right) \tag{18}$$

$$\frac{\partial f^-}{c\partial t} - \frac{\sqrt{\gamma_0^2 - 1}}{\gamma_0}\frac{\partial f^-}{\partial z} + \frac{1}{\gamma_0}\frac{\partial f^+}{\partial z}\exp[i(\omega_0^- - \omega_0^+)t] = i\frac{q}{\hbar}A_z\left(-\frac{\sqrt{\gamma_0^2 - 1}}{\gamma_0}f^- + \frac{1}{\gamma_0}f^+\exp[i(\omega_0^- - \omega_0^+)t]\right) \tag{19}$$

The second terms on the left-hand sides of eqs 18 and 19 represent the propagations of $f^+(z,t)$ and $f^-(z,t)$ with velocities of $v^+ = +c[(\gamma_0^2 - 1)^{1/2}/\gamma_0] = +v_0$ and $v^- = -c[(\gamma_0^2 - 1)^{1/2}/\gamma_0] = -v_0$, respectively. (Note that eqs 18 and 19 are coupled differential equations, and there is no apparent dispersion or ponderomotive terms. It will be shown that those arise from the coupled term.)

Equations 18 and 19 are not directly solvable (to our best knowledge). However, close inspection reveals that an approximation is possible: an approximate solution for $f^-(z,t)$ in eq 19 can be obtained by assuming that the temporal behavior of $f^-(z,t)$ is dominated by the fast oscillation terms, $\exp[-2i\omega_0 t]$, and any cumulated value is rapidly dissipated due to the $-v_0$ propagation term, where $\omega_0 = +\omega_0^+ = -\omega_0^-$. In other words, any change in $f^-(z,t)$ is propagated in the opposite direction from $f^+(z,t)$, and therefore the solution of $f^-(z,t)$ that propagates along with $f^+(z,t)$ is very small and can be approximated (high-frequency approximation) as

$$f^-(z,t) \approx \frac{1}{-2i\omega_0}\frac{c}{\gamma_0}\left(-\frac{\partial f^+}{\partial z} + i\frac{q}{\hbar}A_z f^+\right)e^{-2i\omega_0 t} \tag{20}$$

which approximately satisfies $\partial f^-/\partial t \approx (c/\gamma_0)[-(\partial f^+/\partial z) + i(q/\hbar)A_z f^+]e^{-2i\omega_0 t}$ for very large ω_0 and relatively slowly varying $A_z(z,t)$. An equivalent approximation was obtained in the small kinetic energy limit (nonrelativistic approximation).[24] It is also to be noted that eq 20 with $\vec{A} = 0$ agrees with eq 16 at $t = 0$, since $\hbar\omega_0 = \gamma_0 mc^2$. Using eq 20 in eq 18, we obtain the uncoupled differential equation for $f^+(z,t)$ only as

$$\frac{\partial f^+}{\partial t} + v_0\frac{\partial f^+}{\partial z} - \frac{i\hbar}{2\gamma_0^3 m}\frac{\partial^2 f^+}{\partial z^2} \approx +i\frac{qv_0}{\hbar}A_z f^+ + \frac{qA_z}{\gamma_0^3 m}\frac{\partial f^+}{\partial z} + \frac{q^2 A_z^2}{2i\hbar\gamma_0^3 m}f^+ + \frac{q}{2\gamma_0^3 m}\left(\frac{\partial A_z}{\partial z}\right)f^+ \tag{21}$$

The last term on the right-hand side should vanish for the Coulomb gauge as $\nabla\cdot\vec{A} = 0$ in three dimensions. Then eq 21 restores propagation, dispersion, linear interactions, and ponderomotive terms and is identical to eq 1, the nonrelativistic counterpart, except the relativistic correction, γ_0^3, to the mass in the dispersion and ponderomotive terms (the effective mass becomes the relativistic longitudinal mass,[25] $m_L = \gamma_0^3 m$, whereas the velocity can be related to the transverse mass $m_T = \gamma_0 m = (p_0/v_0)$).

Equation 21 allows us to use the solutions to the Schrödinger equation, with a relativistic correction, such as free wave packet propagation, PINEM effect, and so forth. As with the nonrelativistic formulation in the previous publication, we ignore the dispersion and the ponderomotive terms, and then eq 21 becomes

$$\frac{\partial f^+(z)}{\partial t} + v_0\frac{\partial f^+(z)}{\partial z} \approx +i\frac{qv_0}{\hbar}A_z(z,t)\,f^+(z) \tag{22}$$

which can be transformed to an ordinary differential equation in time at any position for the moving envelope function (equivalent to eq 3), using $g^+(z - v_0 t, t) = f^+(z,t)$ and $z = z' + v_0 t$,

$$\frac{\partial g^+(z')}{\partial t} \approx +i\frac{qv_0}{\hbar}A_z(z' + v_0 t, t)\,g^+(z') \tag{23}$$

dx.doi.org/10.1021/jp304534n | J. Phys. Chem. A 2012, 116, 11128−11133

with a solution (see Supporting Information) giving

$$g^{+}(z', t) = g^{+}(z', t_0) \exp\left[i\frac{qv_0}{\hbar} \int_{t_0}^{t} \mathrm{d}t' \, A_z(z' + v_0 t', t') \right] \tag{24}$$

Equations 22 and 24 are equivalent to the nonrelativistic counterparts (eqs 2 and 4), hence, the classical equivalence (see Supporting Information). The relativistic counterparts to eqs 6 and 7 can be equivalently obtained in the same manner:

$$\frac{g^{+}(z', +\infty)}{g^{+}(z', -\infty)} = \sum_{n=-\infty}^{+\infty} \exp\left[in\frac{\omega_p}{v_0} z' \right] \left(-\frac{\tilde{F}}{|\tilde{F}|} \right)^n J_n\left(\frac{-q}{\hbar\omega_p} |\tilde{F}| \exp\left[-\frac{(z' + v_0\tau)^2}{4{v_0}^2{\sigma_p}^2} \right] \right) \tag{25}$$

The final state wave function is retrieved by substituting $f^{+}(z,t) = g^{+}(z - v_0 t, t)$ in eq 17 at $t \to +\infty$, with $f^{-}(z,t)$ using eq 20 such that

$$\Psi(z, t) = \left\{ g^{+}(z - v_0 t, +\infty) \begin{pmatrix} u_1^{+}(k_0) \\ u_2^{+}(k_0) \end{pmatrix} - \frac{i\hbar}{2{\gamma_0}^2 mc} \frac{\partial g^{+}(z - v_0 t, +\infty)}{\partial z} \begin{pmatrix} u_1^{-}(k_0) \\ u_2^{-}(k_0) \end{pmatrix} \right\} \exp[i(k_0 z - \omega_0^{+} t)] \tag{26}$$

which approximately becomes (see Supporting Information)

$$\Psi(z, t) \approx \sum_{n=-\infty}^{+\infty} \left\{ g_n^{+}(z - v_0 t) \begin{pmatrix} u_1^{+}(k_n) \\ u_2^{+}(k_n) \end{pmatrix} - \frac{i\hbar}{2{\gamma_0}^2 mc} \frac{\partial g_n^{+}(z - v_0 t)}{\partial z} \begin{pmatrix} u_1^{-}(k_n) \\ u_2^{-}(k_n) \end{pmatrix} \right\} \exp[i(k_n z - \omega_n^{+} t)] \tag{27}$$

where $k_n = k_0 + n(\omega_n/v_0)$, $\omega_n^{+} = \omega_0 + n\omega_n$, $g_n^{+}(z') = g^{+}(z', -\infty)\, \xi_n(z')$, and

$$\xi_n(z') = \left(-\frac{\tilde{F}}{|\tilde{F}|} \right)^n J_n\left(\frac{-q}{\hbar\omega_p} |\tilde{F}| \exp\left[-\frac{(z' + v_0\tau)^2}{4v_0^2\sigma_p^2} \right] \right)$$

In momentum space, the wave function becomes

$$\Psi(k) \approx \sum_{n=-\infty}^{+\infty} \mathcal{F}\{g_n^{+}; k - k_n\} \begin{pmatrix} u_1^{+}(k) \\ u_2^{+}(k) \end{pmatrix} \tag{28}$$

The probability of each wavelet becomes

$$P_n \approx \int_{-\infty}^{+\infty} \mathrm{d}k \, |\mathcal{F}\{g_n^{+}; k - k_n\}|^2 \tag{29}$$

Equation 29 is identical to the nonrelativistic counterpart, eq 10.

SUMMARY

In summary, the relativistic formulation of the three-body PINEM, that is, the electron−photon interaction mediated by a nanostructure, was developed and compared to the nonrelativistic counterpart. Solving the Dirac equation is a formidable task, due to the increased degree of freedom (spinor) and the wave function's very high frequency ($|+\omega^{+}| = |-\omega^{-}| \geq mc^2/\hbar$). However, utilizing envelope functions and spinor basis identifies electromagnetic interaction (eqs 18 and 19). Furtherzmore, this very high frequency, which contains mc^2, allows us to obtain an approximate equation and solution of Dirac wave packet equivalent to Schrödinger wave packet (classical correspondence). Using this high-frequency approximation, the Dirac equation for the envelope function of a wave packet under electromagnetic interaction is analytically solved to obtain a first order solution, ignoring the dispersion and the ponderomotive interaction. For the first order solution, the exact equivalence is found and no relativistic correction is required when the relativistic velocity of the electron is used with corresponding classical momentum ($\hbar k_c$) and energy ($\hbar\omega_c$) for the nonrelativistic formulation of the PINEM effect.

dx.doi.org/10.1021/jp304534n | J. Phys. Chem. A 2012, 116, 11128−11133

By utilizing the envelope function, we can separate the change of the wave function due to the electron−photon interaction from that of the initial state wave function. In the Schrödinger and Dirac equations, the (dominant) interaction is consequently identified to be the $\mathbf{v}\cdot q\mathbf{E}$ term. The PINEM field integral in eq 5 is the Fourier transform component of the electric field, but the $\exp[-i\omega_p(z''/v_0)]$ term originates from the separation of the temporal dependence of the scattered wave, that is, $E(z,t) = E(z,0)\exp[-i\omega_p t]$. Therefore, eq 5 is indeed the mechanical work done by the electromagnetic wave on the traveling electron, since $\Delta E = \mathbf{v}\cdot\Delta\mathbf{p} = \mathbf{v}\cdot\int dt q\mathbf{E}(\mathbf{r},t)$ with $z = vt$ (see eqs A.8 in ref 17 and S.13 in the Supporting Information). Because the dispersion relation $\partial E/\partial p = v$ is valid both nonrelativistically and relativistically, the correspondence is found when using the same velocity. Therefore, the results in the nonrelativistic formulation[17] are also valid in the relativistic regime.

■ ASSOCIATED CONTENT

Supporting Information

A detailed derivation of the relativistic probability. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: zewail@caltech.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Science Foundation and the Air Force Office of Scientific Research in the Center for Physical Biology funded by the Gordon and Betty Moore Foundation.

■ REFERENCES

(1) Dirac, P. A. M. *Proc. R. Soc. London, Series A* **1928**, *117*, 610−624.
(2) Thaller, B. *The Dirac equation*; Springer-Verlag: Berlin, 1992.
(3) Gerlach, W.; Stern, O. *Z. Phys.* **1922**, *9*, 349−352.
(4) Anderson, C. D. *Phys. Rev.* **1933**, *43*, 491−494.
(5) Eckart, C.; Griffing, B. L. *Phys. Rev.* **1936**, *50*, 1145−1147.
(6) Bakke, F.; Wergelan, H. *Physica* **1973**, *69*, 5−11.
(7) Krekora, P.; Su, Q.; Grobe, R. *Phys. Rev. Lett.* **2004**, *93*, 043004.
(8) Al-Hashimi, M. H.; Wiese, U. J. *Ann. Phys.* **2009**, *324*, 2599−2621.
(9) Nogami, Y.; Toyama, F. M. *Am. J. Phys.* **2010**, *78*, 176−180.
(10) Gerritsma, R.; Kirchmair, G.; Zahringer, F.; Solano, E.; Blatt, R.; Roos, C. F. *Nature* **2010**, *463*, 68−72.
(11) Volkov, D. M. *Z. Phys.* **1935**, *94*, 250−260.
(12) San Roman, J.; Roso, L.; Reiss, H. R. *J. Phys. B: At., Mol. Opt. Phys.* **2000**, *33*, 1869−1880.
(13) San Roman, J.; Plaja, L.; Roso, L. *Phys. Rev. A* **2001**, *64*, 063402.
(14) San Roman, J.; Roso, L.; Plaja, L. *Laser Phys.* **2005**, *15*, 275−281.
(15) J. Peatross, C. M.; Keitel, C. H. *Opt. Express* **2007**, *15*, 6053−6061.
(16) Boca, M.; Florescu, V. *Eur. Phys. J. D* **2008**, *46*, 15−20.
(17) Park, S. T.; Lin, M.; Zewail, A. H. *New J. Phys.* **2010**, *12*, 123028.
(18) Barwick, B.; Flannigan, D. J.; Zewail, A. H. *Nature* **2009**, *462*, 902−906.
(19) Flannigan, D. J.; Barwick, B.; Zewail, A. H. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 9933−9937.
(20) García de Abajo, F. J.; Kociak, M. *New J. Phys.* **2010**, *10*, 073035.
(21) García de Abajo, F. J.; Asenjo-Garcia, A.; Kociak, M. *Nano Lett.* **2010**, *10*, 1859−1863.
(22) Howie, A. *Eur. Phys. J. Appl. Phys.* **2011**, *54*, 33502.
(23) Abramowitz, M.; Stegun, I. A. *Handbook of Mathematical Functions, with Formulas, Graphs, and Mathematical Tables*; Dover Publications: New York, 1965.
(24) Hamdan, N.; Altorra, A.; Salman, H. A. *Proc. Pak. Acad. Sci.* **2007**, *44*, 263−272.
(25) Lorentz, H. *Proc. K. Ned. Akad. Wet.* **1904**, *6*, 809−831.