# Power-Zienau-Woolley representations of nonrelativistic QED for atoms and molecules

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The interaction terms in the general nonrelativistic Hamiltonian for a collection of spin-free charged particles and the electromagnetic field may be expressed in terms of so-called polarization fields. The general Hamiltonian is related to the familiar Coulomb gauge theory by a family of formally unitary transformations with a line integral over the Coulomb gauge vector potential as generator. The particular choice of a straight-line path starting at an arbitrary origin and ending at a charge defines the Power-Zienau-Woolley transformation; it is commonly approximated by a truncated multipole expansion of the integral about the arbitrary origin. The transformation may be analyzed as a certain kind of coherent state displacement. For an overall neutral many-particle system the paths using the arbitrary origin can be eliminated in favor of paths with end points at the positions of oppositely charged particles. The paths may be interpreted as lines of force in the sense of Faraday, while the polarization fields are just the electromagnetic field strengths for the specified line of force. We develop this line integral representation for the polarization fields and calculate the self-energy of the electric polarization field $\mathbf{P}$ using a straight-line path. For an overall neutral pair of point charges, the energy contributions are their individual (infinite) self-energies, a contact interaction, and a divergent pair term. which together replace the familiar Coulomb interaction. Of course one must not forget also the coupling between $\mathbf{P}$ and the transverse electric field; the paradox is resolved by the requirement for gauge invariance. These results mirror findings in the relatively remote area of high-energy physics where the pairs of oppositely charged particles are typically quark-antiquark partners, and similar line integrals giving the same singular interaction are used.

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## I. INTRODUCTION

The origins of the approach employed in modern atomic and molecular theory can be found in the model of the hydrogen atom proposed by Bohr to account for the spectrum of hydrogen [1,2]. In modern terms the idea is this: Formally, one fixes the gauge of the vector potential $\mathbf{A}$ by the Coulomb gauge condition

$$\nabla \cdot \mathbf{A} = 0 \tag{1}$$

and it then follows that the longitudinal part of the electric field strength due to the electrons and nuclei can be expressed entirely in terms of their coordinates and gives rise to the familiar static Coulomb potential in the QED Hamiltonian. Radiation reaction due to the transverse part of their electromagnetic fields was simply discarded *ad hoc*, and the role of the radiation field was demoted to the status of an external perturbation inducing transitions between Bohr's stationary states. One thus writes the QED Hamiltonian in the Coulomb gauge as

$$\mathsf{H} = \mathsf{H}_{\rm atom} + \mathsf{H}_{\rm rad} + \mathsf{V}_{\rm Cg}, \tag{2}$$

where $\mathsf{H}_{\rm atom}$ is the usual Coulomb Hamiltonian involving purely electrostatic potentials and $\mathsf{V}_{\rm Cg}$ is a definite function of the particle variables and the field potential $\mathbf{A}$.

However, when it is recognized that $\mathsf{H}$ refers to a closed system of charges and electromagnetic fields, the situation is complicated by the requirement for gauge invariance of physical quantities. The clean separation of field and atomic contributions in (2) is peculiar to the Coulomb gauge. In general, a decomposition of the QED Hamiltonian analogous to (2) in an arbitrary gauge with the usual atomic Hamiltonian explicit contains arbitrary quantities in the interaction $\mathsf{V}$, expressed through so-called polarization fields [3]. This feature of QED is made explicit by a unitary transform of $\mathsf{H}_{\rm Cg}$, an example of which is the Power-Zienau-Woolley (PZW) transformation. The most important fact about the polarization fields is that they are not measurable physical quantities; they occur as useful working variables, like the field potentials. This is because no specific choice of the polarization fields corresponds to a definite physical situation; the corollary is that any calculation of a physical quantity must be independent of the choice of the polarization fields used to make the calculation.

The transformation was first proposed for an investigation of the interaction energy of two neutral atoms in a cavity using QED within the dipole approximation [4]. In the Coulomb gauge the interaction is mediated by a propagator of the transverse vector potential and the Coulomb interaction energy. The propagator in momentum space has a pole at $|\mathbf{k}| = 0$ which, after Fourier transformation, leads to a static term in real space even though the retarded boundary condition is

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used. The static term cancels precisely with the *interatomic* Coulomb energies to leave an overall retarded result, so that the interatomic interaction can be described as resulting from the exchange of purely transverse photons.[1] Another account of the transformation was given shortly afterward with the resulting Hamiltonian used to investigate line shapes [5]. Later a more complete treatment of the transformation for cavity QED was given and used to study atoms near a conducting wall [6]. The general belief that the contribution to the Hamiltonian of the term $\int |\mathbf{P}^{\perp}|^2 d^3\mathbf{x}$ amounts to only self-energies and contact interaction terms, and so may usually be ignored, originated in these investigations based on the dipole approximation. Since that early work, PZW ideas have spread into numerous areas of atomic/molecular/optical physics; contemporary references can be found in recent surveys [7,8]; PZW ideas have also been of value in QED studies in condensed matter physics [9,10].

Since it is concerned with atoms and molecules in terms of electrons and nuclei, and radiation, the framework for QED used here is nonrelativistic, and the question arises whether or how a secure mathematical version can be formulated in the nonrelativistic framework. There are questions that have not been answered in the conventional perturbation theory ($S$-matrix) formulation of Lorentz invariant QED, for example, the stability of matter [11–13], but these concerns apply also in atomic/molecular spectroscopy. Among the issues that should be mentioned are the Hilbert space to be used [14–17], the maintenance of gauge invariance in calculations of physical observables, the role of the Coulomb interaction associated uniquely with the Coulomb gauge condition, and the occurrence of singular contributions to the potential $\mathsf{V}$ in the nonrelativistic QED Hamiltonian. In order to attack these questions it is essential to have a comprehensive account of the nonrelativistic theory before any other approximations are made. The present paper is a contribution to that goal. It will become apparent that the use of the electric dipole approximation, often combined with a few atomic states, apparently essential for many practical calculations, can lead to theoretical results that are not found in the general theory presented here.

The use of the conventional Fock space structure requires the imposition of a cutoff on the magnitude of the photon momentum in the interaction terms; this is the usual step, normally restricted to the Coulomb gauge formalism, in the mathematical physics literature (see, for example, [12,13,18]). Even so, a moving charge interacting with the quantized field gives rise to an infrared divergence in a free-field Fock space description [16,17]. The motivation for the transformation discussed here is the recognition that physically, charged particles cannot be separated from electromagnetic fields in the way that is suggested by the Coulomb gauge theory if an atomic system as a whole is to be incorporated properly in the field as a source (the original idea of Power and Zienau [4,5]).

The outline of the paper is as follows. In Sec. II we summarize the context for the transformation that expresses a formal relationship between the familiar Coulomb gauge Hamiltonian and the general Hamiltonian; the PZW transformation is a special case. In Sec. III the expression of the polarization fields in terms of line integrals for multiparticle systems is developed without reference to arbitrary multipole origins. In Sec. IV the self-energy contribution of the polarization field $\mathbf{P}$ to the energy of the total system is investigated and shown to be highly singular in an unexpected way that was not recognized in the original literature [19–24]. This calculation shows that the *whole* Coulomb energy, intra-atomic and interatomic, is canceled, leaving only singular terms. In principle, since the transformation is canonical the energy has simply been rearranged and the equations of motion are not disturbed. In Sec. V the relationship between the PZW Hamiltonian (3) and the Coulomb gauge theory is represented as a coherent state displacement transformation (boson translation). This approach leads directly to an evaluation of the overlap between the Fock space vacuum of the Coulomb gauge theory and the transformed vacuum. In the continuum limit and for point particles, this overlap is zero, implying that the transformed Hamiltonian cannot be discussed in the same Fock space as the Coulomb gauge theory because they are not unitarily equivalent. Section VI provides an interpretation of the polarization fields in terms of lines of force, which is related to recent work in high-energy physics [25,26]. The paper concludes with a summary in Sec. VII.

## II. THE PZW HAMILTONIAN

For a closed system of $N \geqslant 1$ spinless charges in a radiation field $(\mathbf{E}^{\perp}, \mathbf{B})$, the general nonrelativistic Hamiltonian for electrodynamics may be written

$$\begin{aligned}\mathsf{H}_{\mathbf{P}} = &\sum_{n=1}^{N} \frac{|\mathbf{p}_n|^2}{2m_n} + \frac{1}{2}\epsilon_0 \int (|\mathbf{E}^{\perp}|^2 + c^2|\mathbf{B}|^2) d^3\mathbf{x} \\ &- \int \mathbf{P}\cdot\mathbf{E}^{\perp} d^3\mathbf{x} - \int \mathbf{M}\cdot\mathbf{B}\, d^3\mathbf{x} + \iint \boldsymbol{\mathcal{X}} : \mathbf{B}\mathbf{B}\, d^3\mathbf{x}\, d^3\mathbf{x}' \\ &+ \frac{1}{2\epsilon_0}\int \mathbf{P}\cdot\mathbf{P}\, d^3\mathbf{x} \end{aligned} \tag{3}$$

in the usual notation [7]. The nonzero commutators are

$$\left[\mathsf{x}_n^i, \mathsf{p}_m^j\right] = i\hbar\delta_{ij}\delta_{nm}, \tag{4}$$

$$[\mathsf{E}(\mathbf{x})_k^{\perp}, \mathsf{B}(\mathbf{x}')_l] = i\hbar\epsilon_0^{-1}\epsilon_{klm}\nabla_{\mathbf{x}}^m \delta^3(\mathbf{x}-\mathbf{x}'), \tag{5}$$

corresponding to the conventional assumption that the field and particle variables are independent. The general Hamiltonian has this form for both classical electrodynamics and QED, the difference being only in the interpretation of the dynamical variables as classical quantities or as operators on a Hilbert space. In both cases Hamilton's equations lead to the Maxwell equations and the Lorentz force law. Its extension to nonrelativistic electrons and nuclei follows from implementation of the permutation symmetry for identical particles in quantum mechanics. Additionally, the Pauli interaction coupling particle spins to the magnetic field with phenomenological nuclear magnetic moments can properly be regarded as a nonrelativistic contribution to the QED

[1] In the language of covariant QED, the transformation has eliminated both scalar and longitudinal photons.

Hamiltonian for electrons and nuclei and may be incorporated in the magnetization $\mathbf{M}$ if required.

In (3) the first term is the total kinetic energy for $N$ free charges and the second term is the usual Hamiltonian for free radiation. The next three terms couple the charges to the radiation, while the last term has no dependence on the field or on the particle's motion; it is of a purely kinematic nature. Further, $\mathbf{M}$ is a magnetization density linear in the charge $e$ that involves the particle position and momentum variables and $\boldsymbol{\mathcal{X}}$ is a generalized diamagnetic susceptibility tensor that is proportional to $e^2$. Their particular forms depend on the choice made for the electric polarization field $\mathbf{P}$, which is also linear in the charge $e$. No assumption is made as to whether the charges are localized in one or more bounded regions of space.

The Hamiltonian (3) and the familiar Coulomb gauge Hamiltonian $\mathsf{H}_{\rm Cg}$ (discussed below) are intertwined by the formally unitary operator

$$\mathsf{U}_{\mathbf{P}} = \exp(i\Lambda_{\mathbf{P}}/\hbar), \tag{6}$$

where the generator is a functional scalar product with the dimensions of action

$$\Lambda_{\mathbf{P}} = \int \mathbf{P}\cdot\mathbf{A}\, d^3\mathbf{x}. \tag{7}$$

Here $\mathbf{A}$ is specifically the Coulomb gauge vector potential for the field and $\mathbf{P}$ is required to satisfy the relation

$$\nabla\cdot\mathbf{P} = -\rho. \tag{8}$$

Thus the relations

$$\mathsf{H}_{\mathbf{P}} = \mathsf{U}_{\mathbf{P}}^{-1}\mathsf{H}_{\rm Cg}\mathsf{U}_{\mathbf{P}}, \tag{9}$$

$$\Psi_{\mathbf{P}} = \mathsf{U}_{\mathbf{P}}^{-1}\Psi_{\rm Cg} \tag{10}$$

define a new representation for nonrelativistic QED. Obviously $\mathsf{U}_{\mathbf{P}}$ commutes with $\mathbf{A}$, so $\mathbf{A}$ is unchanged by the transformation, which is not a gauge transformation.

The PZW Hamiltonian is obtained by expressing the electric polarization field in terms of line integrals over Dirac $\delta$ functions with a particular choice of path [19–24]. With this choice the building block of the generator (7) is a line integral over the vector potential

$$\Lambda_{\rm PZW} \sim e\int_C \mathbf{A}(\mathbf{z})\cdot d\mathbf{z}, \tag{11}$$

where $C$ is a *straight-line* path ending at a charge $e$; the generalization to many charges is

$$\Lambda_{\rm PZW} = \sum_{n=1}^{N} e_n \int_{C_n} \mathbf{A}(\mathbf{z})\cdot d\mathbf{z} \tag{12}$$

over paths $\{C_n\}$ terminating at the positions $\{\mathbf{x}_n\}$. Comparison with (7) shows that the polarization field in the PZW formalism may be written as the distribution

$$\mathbf{P}(\mathbf{x}) = \sum_{n=1}^{N} e_n \int_{C_n} \delta^3(\mathbf{x}-\mathbf{z})d\mathbf{z}. \tag{13}$$

The specification of the starting points of the paths will be discussed in Sec. III, where it is verified that such a form satisfies (8) with the usual charge density distribution

$$\rho(\mathbf{x}) = \sum_{n=1}^{N} e_n\delta^3(\mathbf{x}-\mathbf{x}_n). \tag{14}$$

Equation (11) may be viewed as an integrated form derived from the infinitesimal version of the fundamental quantum-mechanical law of electromagnetism [27] in terms of the 1-form $d\omega = \mathbf{a}\cdot d\mathbf{z}$ (the connection of Abelian gauge theory). The transformation is carried out explicitly and in closed form using the power series expansion of the exponential operator $\mathsf{U}_{\mathbf{P}}$ [4,5,20,28].

Equation (8) does not fix $\mathbf{P}$ uniquely, so we may consider using a path different from the PZW choice and a modified generator operator $\Lambda_{\mathbf{P}'}$. The result of transforming the Coulomb gauge Hamiltonian $\mathsf{H}_{\rm Cg}$ with the modified operator $\mathsf{U}_{\mathbf{P}'}$ can be put in the form

$$\mathsf{H}_{\mathbf{P}'} = \mathsf{U}_{\mathbf{P}'}^{-1}\mathsf{H}_{\rm Cg}\mathsf{U}_{\mathbf{P}'} = \mathsf{U}_{\mathbf{B}}^{-1}\mathsf{H}_{\mathbf{P}}\mathsf{U}_{\mathbf{B}}, \tag{15}$$

where for each charge $e$,

$$\mathsf{U}_{\mathbf{B}} = \exp\left(-\frac{ie}{\hbar}\oint \mathbf{A}(\mathbf{z})\cdot d\mathbf{z}\right) \equiv \exp\left(-\frac{ie}{\hbar}\int_{\Sigma} d\mathbf{S}\cdot\mathbf{B}\right). \tag{16}$$

Here $\Sigma$ is a surface with the closed loop as its boundary, which has the PZW path as a segment, and $\mathsf{H}_{\mathbf{P}}$ is the PZW Hamiltonian; Eqs. (11) and (16) will be recognized as a Wilson line and a Wilson loop, respectively [29].

Although (16) is gauge invariant, $\mathsf{U}_{\mathbf{B}}$ still has an implicit dependence on the paths chosen through their definition of the surface $\Sigma$; it is independent of the particle variables, although it depends on the charge parameter $e$, so that the PZW forms for the polarization fields $\mathbf{P}$ and $\mathbf{M}$ and the susceptibility $\boldsymbol{\mathcal{X}}$ can be left unchanged. However, the transformed Hamiltonian $\mathsf{H}_{\mathbf{P}'}$ for the altered path differs from $\mathsf{H}_{\mathbf{P}}$ because of the noncommutation of $\mathsf{U}_{\mathbf{B}}$ with $\mathbf{E}^{\perp}$, and additional terms arise from the second and third terms in (3). This aspect will not be pursued here; in the following we confine attention to the PZW choice of path and simply emphasize that any calculation of a physical quantity must not depend on the choice of path.

Choosing $\mathbf{P} = \mathbf{P}^{\parallel}$ and $\mathbf{P}^{\perp} = 0$ in (7) makes $\Lambda_{\mathbf{P}^{\parallel}} = 0$ since $\mathbf{A}$ is purely transverse. Then $\mathsf{U}_{\mathbf{P}} = \mathsf{I}$, the identity, and (3) is simply the usual Coulomb gauge Hamiltonian; the third term vanishes, the fourth and fifth terms become the familiar $\mathbf{p}\cdot\mathbf{A}$ and $|\mathbf{A}|^2$ interactions, and the last term reduces to the Coulomb energies of pairs of charges and their infinite self-energies. Thus we have

$$\begin{aligned}\mathsf{H}_{\rm Cg} = &\sum_{n=1}^{N}\frac{|\mathbf{p}_n|^2}{2m_n} + \frac{1}{2\epsilon_0}\int \mathbf{P}^{\parallel}\cdot\mathbf{P}^{\parallel}d^3\mathbf{x}\\ &+\frac{1}{2}\epsilon_0\int(|\mathbf{E}^{\perp}|^2 + c^2|\mathbf{B}|^2)d^3\mathbf{x}\\ &-\sum_{n=1}^{N}\frac{e_n}{m_n}\mathbf{p}_n\cdot\mathbf{A}(\mathbf{x}_n) + \sum_{n=1}^{N}\frac{e_n^2}{2m_n}\mathbf{A}(\mathbf{x}_n)\cdot\mathbf{A}(\mathbf{x}_n).\end{aligned} \tag{17}$$

The identification with (2) is immediate if we use the relation [20]

$$\frac{1}{2\epsilon_0}\int \mathbf{P}^{\parallel}\cdot\mathbf{P}^{\parallel}d^3\mathbf{x} \equiv \frac{1}{8\pi\epsilon_0}\sum_{n,m=1}^{N}\frac{e_n e_m}{|\mathbf{x}_n-\mathbf{x}_m|}. \tag{18}$$

The nonzero commutators are

$$\left[\mathsf{x}_n^r, \mathsf{p}_m^s\right] = i\hbar\delta_{nm}\delta_{rs}, \tag{19}$$

$$[\mathsf{A}(\mathbf{x},t)^r, \mathsf{E}(\mathbf{x}',t)^{\perp s}] = -i\hbar\epsilon_0^{-1}\delta_{rs}^{\perp}(\mathbf{x}-\mathbf{x}'), \tag{20}$$

It will be seen in Sec. IV that in (3), unlike (17), there are in general no explicit static Coulomb interaction energies between the charges which must arise from the charge-field interaction terms and the last term in (3).

## III. LINE INTEGRAL FORMS FOR THE POLARIZATION FIELDS

The traditional idea of the polarization field is to replace the charge-current density 4-vector $j^\mu = (c\rho, \mathbf{j})$ with a second-rank tensor density $p^{\mu\nu}$ through the relation

$$j^\mu = \partial_\nu p^{\mu\nu} \tag{21}$$

so as to construct the classical displacement fields for dielectric theory with the combination

$$d^{\mu\nu} = cf^{\mu\nu} + (c\epsilon_0)^{-1}p^{\mu\nu}, \tag{22}$$

where $f^{\mu\nu}$ is the usual Faraday tensor for the electromagnetic field. The inner product $\epsilon_0 d_{\mu\nu}d^{\mu\nu}$ is an energy density. Provided $p^{\mu\nu}$ is antisymmetric and single valued, the equation of continuity is satisfied automatically,

$$\partial_\mu j^\mu = \partial_\mu\partial_\nu p^{\mu\nu} = 0. \tag{23}$$

An antisymmetric second-rank tensor has six independent components in $d = 4$ dimensions which can be identified as the components of a pair of vectors. The tensor $p^{\mu\nu}$ in $(4\times 4)$ matrix form is

$$p^{\mu\nu} = \begin{pmatrix} 0 & -cP_x & -cP_y & -cP_z \\ cP_x & 0 & M_z & -M_y \\ cP_y & -M_z & 0 & M_x \\ cP_z & M_y & -M_x & 0 \end{pmatrix}, \tag{24}$$

where $\{P_r\} = \mathbf{P}$ is the electric polarization field and $\{M_r\} = \mathbf{M}$ is the magnetization (magnetic polarization) field [19]. Now (21) is of the same form as the Maxwell equations

$$\partial_\nu f^{\mu\nu} = \mu_0 j^\mu \tag{25}$$

for a specified charge-current density. Thus $p^{\mu\nu}$ is an electromagnetic field associated specifically with the current $j^\mu$; however, $p^{\mu\nu}$ is not required to satisfy the other Maxwell equations,

$$\partial_\alpha f_{\beta\gamma} + \partial_\beta f_{\gamma\alpha} + \partial_\gamma f_{\alpha\beta} = 0, \tag{26}$$

and so it is not necessarily the Maxwell field, and no particular form can be associated with a given physical situation.

The Green's function $\mathbf{g}(\mathbf{x},\mathbf{x}')$ for the divergence operator satisfies

$$\nabla_x\cdot\mathbf{g}(\mathbf{x},\mathbf{x}') = -\delta^3(\mathbf{x}-\mathbf{x}'). \tag{27}$$

The longitudinal component of $\mathbf{g}$ is well defined; it can be written as

$$\mathbf{g}(\mathbf{x},\mathbf{x}')^{\parallel} = \nabla_{\mathbf{x}}\frac{1}{4\pi|\mathbf{x}-\mathbf{x}'|}. \tag{28}$$

A more general choice for $\mathbf{g}$ is based on direct integration of (27). This is the path-dependent representation

$$\mathbf{g}(\mathbf{x},\mathbf{x}';\mathbf{O},C) = \mathbf{g}(\mathbf{x},\mathbf{O})^{\parallel} + \int_C^{\mathbf{x}'}\delta^3(\mathbf{z}-\mathbf{x})d\mathbf{z}, \tag{29}$$

which has a transverse component as well as the longitudinal component (28). Here $C$ is any suitable curve starting from a fixed point $\mathbf{O}$ and ending at the space point $\mathbf{x}'$ such that the integral exists; $\mathbf{g}(\mathbf{x},\mathbf{O})^{\parallel}$ is an integration constant which may be dropped if $\mathbf{O}$ is chosen as spatial infinity. Equation (29) is to be understood [25] as a distribution in the variable $\mathbf{x}$. A physical interpretation of $\mathbf{g}(\mathbf{x},\mathbf{x}')$ is given in Sec. VI. Using $\mathbf{g}$, we may construct a formal integral representation of the electric polarization field

$$\mathbf{P}(\mathbf{x}) = \int \mathbf{g}(\mathbf{x},\mathbf{x}')\rho(\mathbf{x}')d^3\mathbf{x}'. \tag{30}$$

Consider first the polarization field for a single charge at $\mathbf{X}$ for which the natural origin $\mathbf{O}$ is a point at infinity. Using (14) with the path $\mathbf{z}(\sigma) = \mathbf{X} + \sigma\hat{\mathbf{n}}$, $-\infty \leqslant \sigma \leqslant 0$, i.e., along a straight path from infinity to the point $\mathbf{X}$, the polarization field is

$$\mathbf{P}(\mathbf{x}) = e\hat{\mathbf{n}}\int_{-\infty}^{0}\delta^3(\mathbf{z}(\sigma)-\mathbf{x})d\sigma. \tag{31}$$

The *mean value* of this polarization field is an unweighted average over all the lines of force. Proceeding to the continuum limit, this is

$$\langle\mathbf{P}(\mathbf{x})\rangle_{\hat{\mathbf{n}}} = \frac{1}{4\pi}\int\mathbf{P}(\mathbf{x})d\Omega. \tag{32}$$

The paths within the infinitesimal solid angle $d\Omega$ will fill up a cone at the position $\mathbf{X}$ with volume elements $d^3\mathbf{z} = r^2 dr d\Omega$, where $r = |\mathbf{z}-\mathbf{X}|$. Equation (32) is easily evaluated using an argument given by Belinfante [30], with the result that

$$\langle\mathbf{P}(\mathbf{x})\rangle_{\hat{\mathbf{n}}} = \mathbf{P}(\mathbf{x})^{\parallel}. \tag{33}$$

From (28) and (30) one sees that the *mean* electric polarization field is just the usual static Coulombic potential of the charge.

This result generalizes directly to the many-charge case for which the electric polarization field is

$$\mathbf{P}(\mathbf{x}) = q\mathbf{g}(\mathbf{x},\mathbf{O})^{\parallel} + \sum_{n=1}^{N}e_i\int_{\mathcal{C}_n}^{\mathbf{x}_n}\delta^3(\mathbf{z}-\mathbf{x})d\mathbf{z}, \quad q = \sum_{n=1}^{N}e_n. \tag{34}$$

If the atom/molecule is overall neutral, $q = 0$ and the arbitrary integration constant plays no role. The arbitrary origin however still appears as an end point in the line integrals. In the case of an overall electrically neutral collection of electrons and nuclei it may be removed by rearranging the charge density to be used in (30) in the following way.

Suppose there are altogether $M$ nuclei with positive charges $\{eZ_a : a = 1,\ldots,M\}$; then there must be $K = MZ_a$ electrons with charge $-e$ to give electroneutrality. Let the nuclei have coordinates $\{\mathbf{x}_m^N : m = 1,\ldots,M\}$; similarly, the

electrons have coordinates $\{\mathbf{x}_k^e : k = 1, \ldots, K\}$. Now write the charge density as a sum of contributions from individual electrons and nuclei

$$\begin{aligned}\rho &= \sum_n e_n \delta^3(\mathbf{x} - \mathbf{x}_n) = \rho(\mathbf{x})^N + \rho(\mathbf{x})^e \\ &= eZ_1\delta^3\big(\mathbf{x} - \mathbf{x}_1^N\big) + eZ_2\delta^3\big(\mathbf{x} - \mathbf{x}_2^N\big) + \cdots \\ &\quad + eZ_M\delta^3\big(\mathbf{x} - \mathbf{x}_M^N\big) - e\delta^3\big(\mathbf{x} - \mathbf{x}_1^e\big) \\ &\quad - e\delta^3\big(\mathbf{x} - \mathbf{x}_2^e\big) - \cdots - e\delta^3\big(\mathbf{x} - \mathbf{x}_K^e\big). \end{aligned} \tag{35}$$

Next take the terms for the nuclei and rewrite them as

$$\begin{aligned}\rho(\mathbf{x})^N &= e\Big[\underbrace{\delta^3\big(\mathbf{x} - \mathbf{x}_1^N\big) + \cdots \delta^3\big(\mathbf{x} - \mathbf{x}_1^N\big)}_{Z_1 \text{ terms}}\Big] \\ &\quad + \cdots + e\Big[\underbrace{\delta^3\big(\mathbf{x} - \mathbf{x}_M^N\big) + \cdots + \delta^3\big(\mathbf{x} - \mathbf{x}_M^N\big)}_{Z_M \text{ terms}}\Big]. \end{aligned} \tag{36}$$

There are now altogether $K$ terms with coefficient $+e$ which can be paired off with the $K$ terms with coefficient $-e$, so the charge density can be rearranged to the form

$$\begin{aligned}\rho(\mathbf{x}) &= e\big[\delta^3\big(\mathbf{x} - \mathbf{x}_1^N\big) - \delta^3(\mathbf{x} - \mathbf{x}_1^e)\big] \\ &\quad + e\big[\delta^3\big(\mathbf{x} - \mathbf{x}_1^N\big) - \delta^3\big(\mathbf{x} - \mathbf{x}_2^e\big)\big] + \cdots \\ &\quad + e\big[\delta^3\big(\mathbf{x} - \mathbf{x}_M^N\big) - \delta^3\big(\mathbf{x} - \mathbf{x}_K^e\big)\big] \\ &= e\sum_{m=1}^{M}\sum_{k=1}^{Z_m}\big[\delta^3\big(\mathbf{x} - \mathbf{x}_m^N\big) - \delta^3\big(\mathbf{x} - \mathbf{x}_{mk}^e\big)\big]. \end{aligned} \tag{37}$$

Combining the charge density (37) with (30) yields the polarization field for an overall neutral multiparticle system as

$$\mathbf{P}(\mathbf{x}) = e\sum_{m=1}^{M}\sum_{k=1}^{Z_m}\mathcal{G}\big(\mathbf{x}; \mathbf{x}_m^N, \mathbf{x}_{mk}^e\big), \tag{38}$$

where

$$\mathcal{G}\big(\mathbf{x}; \mathbf{x}_m^N, \mathbf{x}_{mk}^e\big) = \int_{\mathbf{x}_{mk}^e}^{\mathbf{x}_m^N} \delta^3(\mathbf{z} - \mathbf{x})d\mathbf{z} \tag{39}$$

is independent of the arbitrary origin $\mathbf{O}$ and the integral is taken over any path $\mathcal{C}$ from the point $\mathbf{x}_{mk}^e$ to the position $\mathbf{x}_m^N$. Thus the general polarization field may be written formally as a sum of atomic contributions

$$\mathbf{P}(\mathbf{x}) = \sum_{m=1}^{M}\mathbf{P}_m(\mathbf{x}), \quad \mathbf{P}_m(\mathbf{x}) = e\sum_{k=1}^{Z_m}\int_{\mathbf{x}_{mk}^e}^{\mathbf{x}_m^N}\delta^3(\mathbf{z} - \mathbf{x})d\mathbf{z}. \tag{40}$$

A typical term in (40) is

$$\mathbf{P}(\mathbf{x}, C) = e\int_{\mathbf{x}_1}^{\mathbf{x}_2}\delta^3(\mathbf{x} - \mathbf{z})d\mathbf{z} \tag{41}$$

along some path $\mathcal{C}$; this is the main case we discuss. The Fourier transform of this electric polarization field is

$$\mathbf{P}(\mathbf{k}, C) = e\int_{\mathbf{x}_1}^{\mathbf{x}_2} e^{i\mathbf{k}\cdot\mathbf{z}}d\mathbf{z}. \tag{42}$$

The straight line starting at $\mathbf{x}_1$ and ending at $\mathbf{x}_2$ may be given the parametric form

$$\mathbf{z}(\sigma) = \mathbf{x}_1 + \sigma(\mathbf{x}_2 - \mathbf{x}_1), \quad 0 \leqslant \sigma \leqslant 1. \tag{43}$$

The explicit evaluation of the Fourier transform (42) for this path then yields

$$\mathbf{P}(\mathbf{k}, C) = ee^{i\mathbf{k}\cdot\mathbf{x}_1}\frac{e^{i\mathbf{k}\cdot\mathbf{r}} - 1}{i\mathbf{k}\cdot\mathbf{r}}\mathbf{r}, \tag{44}$$

where $\mathbf{r} = \mathbf{x}_2 - \mathbf{x}_1$; for $\mathbf{k} \to 0$ and finite $|\mathbf{r}|$ this leads to the dipole approximation for the electric polarization field

$$\lim_{\mathbf{k}\to 0}\mathbf{P}(\mathbf{k}, C) = e(\mathbf{x}_2 - \mathbf{x}_1) \equiv \mathbf{d}. \tag{45}$$

For infinite paths the limit does not exist in general and there is no dipole approximation. So far nothing has been said about time dependence. If the charges are allowed to move there is also a current density and one requires the magnetization $\mathbf{M}$. The companion to (41) is

$$\mathbf{M}(\mathbf{x}, t) = e\int_{\mathbf{x}_1}^{\mathbf{x}_2}\delta^3(\mathbf{z} - \mathbf{x})d\mathbf{z} \wedge \dot{\mathbf{z}}, \tag{46}$$

which generalizes directly to the many-charge case.

The forms (41) and (46) for the polarization fields can be obtained directly from recent results in relativistic electrodynamics by reduction to the nonrelativistic limit without any analogies to the classical dielectric theory. A path[2] between two charges can be described in parametrized form such that the boundary values of the parameter, say, $\sigma$, give the positions of the two particles. If the particles move, so does this path, which sweeps out a two-dimensional surface describable by functions $X^\mu(\tau, \sigma)$, $\mu = 0$–3. The tensor

$$p^{\mu\nu}(Y) = -e\int d\tau\, d\sigma\left(\frac{\partial X^\mu}{\partial\sigma}\frac{\partial X^\nu}{\partial\tau} - \frac{\partial X^\nu}{\partial\sigma}\frac{\partial X^\mu}{\partial\tau}\right)\delta^4(X - Y) \tag{47}$$

satisfies Eq. (21) with the current density for an overall neutral pair of particles [25]

$$j^\mu = e\int_{-\infty}^{+\infty}\dot{X}_1\delta^4(X - X_1)dt - e\int_{-\infty}^{+\infty}\dot{X}_2\delta^4(X - X_2)dt. \tag{48}$$

Following the discussion above, the tensor $p^{\mu\nu}$ with components defined by (47) describes the electromagnetic field associated with the path connecting the particle positions.

For the reduction to nonrelativistic form we choose the static gauge with $\tau = t$, where $t$ is physical time [31]. Then, since

$$\left(\frac{\partial X^\mu}{\partial\sigma}\right) = \left(\frac{\partial X^0}{\partial\sigma}, \frac{\partial\mathbf{X}}{\partial\sigma}\right) \equiv \left(0, \frac{\partial\mathbf{X}}{\partial\sigma}\right), \tag{49}$$

$$\left(\frac{\partial X^\mu}{\partial\tau}\right) = \left(\frac{\partial X^0}{\partial t}, \frac{\partial\mathbf{X}}{\partial t}\right) \equiv \left(c, \frac{\partial\mathbf{X}}{\partial t}\right), \tag{50}$$

the corresponding polarization fields that represent the nonrelativistic forms of the current density (48) are just (41) and (46) with $\mathbf{X}$ identified with $\mathbf{z}$.

[2]The path between two charges must not be confused with the world line of an individual charge.

## IV. ENERGY OF THE ELECTRIC POLARIZATION FIELD

The general Hamiltonian (3) contains terms that are either linear or quadratic in the polarization fields; the linear terms represent formally the interactions of individual atoms or groups with the radiation field, and using (40), the last, quadratic, term may be decomposed into a sum of atomic terms, associated with a single nucleus and a sum over the pairwise cross terms, involving two distinct nuclei

$$\mathcal{E}_{\mathbf{P}} = \frac{1}{2\epsilon_0}\int \mathbf{P}(\mathbf{x})\cdot\mathbf{P}(\mathbf{x})d^3\mathbf{x} = \frac{1}{2\epsilon_0}\int \sum_m^M |\mathbf{P}_m(\mathbf{x})|^2 d^3\mathbf{x} + \frac{1}{2\epsilon_0}\int \sum_{m\neq m'}^M \mathbf{P}_m(\mathbf{x})\cdot\mathbf{P}_{m'}(\mathbf{x})d^3\mathbf{x}. \tag{51}$$

These sums must be further differentiated as there are three kinds of terms to evaluate as follows: type 1 terms that refer to one nucleus and one electron as described in Sec. III, type 2 terms that refer to one nucleus and two electrons, and type 3 terms that refer to two different nuclei and two electrons.

Using the Fourier transform of $\mathbf{P}$, we may write

$$\mathcal{E}_{\mathbf{P}} = \frac{1}{2\epsilon_0}\frac{1}{(2\pi)^3}\int \mathbf{P}(\mathbf{k})\cdot\mathbf{P}(-\mathbf{k})d^3\mathbf{k}, \tag{52}$$

which will be used for calculation. That (51) gave a singular contribution to the Hamiltonian was noted in early discussions of the electrodynamics of atoms and molecules [5,28,32], although its properties were characterized poorly when recourse was taken to the conventional multipole expansions of the electric polarization field. The main difficulty is that for point charges the electric polarization field is the distribution (34) and the product of distributions is not well defined. The regularization of the singular expressions that arise in nonrelativistic electrodynamics can be interpreted in terms of a smoothing of the $\delta$ functions in (14). It may then be possible to isolate finite contributions (if any) that survive when the regulator is removed; however, the coefficients of terms that become singular when the $\delta$ function limit is taken generally depend on the chosen regulator function and are not trustworthy.

We imagine that the charge density of a particle is centered on the position $\mathbf{X}$ and write

$$\rho(\mathbf{x}) = e\xi_a(\mathbf{x}-\mathbf{X}), \quad \xi_a(\mathbf{x}) \geqslant 0, \tag{53}$$

with $\xi_a$ a spherically symmetric function, normalized such that

$$\int \xi_a d^3\mathbf{x} = 1. \tag{54}$$

Let $\chi_a(k)$ be the Fourier transform of $\xi_a(\mathbf{x})$; it depends on only $k = |\mathbf{k}|$, and the properties

$$|\chi_a(k)| \leqslant 1, \quad \chi_a(0) = \chi_0(k) = 1, \quad \int_0^\infty \chi_a^2(k)dk = \frac{\pi}{2a} \tag{55}$$

ensure that the usual classical point-particle results are recovered in the limit $a \to 0$.

As a prototypical example, consider the longitudinal component of the polarization field for a single distributed charge $e$ located at $\mathbf{X}$, which is

$$\mathbf{P}_a(\mathbf{x})^{\parallel} = e\int \mathbf{g}(\mathbf{x},\mathbf{x}')\xi_a(\mathbf{x}')d^3\mathbf{x}', \tag{56}$$

as follows from (28) and (53). The Fourier transform of (56) is

$$\mathbf{P}_a(\mathbf{k})^{\parallel} = -ie\mathbf{k}e^{i\mathbf{k}\cdot\mathbf{X}}\frac{\chi_a(k)}{k^2}, \tag{57}$$

so that

$$\mathcal{E}^{\parallel}_{\mathbf{P},a} = \frac{e^2}{2\epsilon_0}\frac{1}{(2\pi)^3}\int \frac{\chi_a^2(k)}{k^2}d^3\mathbf{k} = \frac{e^2}{8\pi\epsilon_0 a}. \tag{58}$$

In the limiting case of the point particle ($a \to 0$), this is the familiar classical infinite Coulombic self-energy.

For the neutral two-particle system discussed earlier (Sec. III) there is only the type 1 contribution

$$\mathcal{E}_{\mathbf{P}} = \frac{e}{2\epsilon_0}\int_{\mathbf{x}_1}^{\mathbf{x}_2}\mathbf{P}(\mathbf{z})\cdot d\mathbf{z}, \tag{59}$$

with $\mathbf{P}$ given by (41); $\mathcal{E}_{\mathbf{P}}$ in general is path dependent. In the following we calculate it for the straight-line path between $\mathbf{x}_1$ and $\mathbf{x}_2$ using the Fourier transform (44). The longitudinal and transverse contributions to $\mathcal{E}_{\mathbf{P}}$ can be identified by introducing a resolution of the identity into (52) to separate the scalar product with

$$\mathbf{I} = \hat{\mathbf{k}}\hat{\mathbf{k}} + (\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}). \tag{60}$$

The regulated longitudinal contribution from (59) is then

$$\mathcal{E}^{\parallel}_{\mathbf{P},a} = \left(\frac{e^2}{4\pi\epsilon_0}\right)\left(\frac{1}{2\pi^2}\right)\int \chi_a^2(k)\frac{1-\cos(\mathbf{k}\cdot\mathbf{r})}{k^2}d^3\mathbf{k}. \tag{61}$$

Integrating over the angles results in

$$\mathcal{E}^{\parallel}_{\mathbf{P}} = \frac{e^2}{2\pi^2\epsilon_0}\lim_{a\to 0}\int_0^\infty \chi_a^2(k)\left(1-\frac{\sin(kr)}{kr}\right)dk = \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{a}\bigg|_{a\to 0} - \frac{1}{r}\right), \tag{62}$$

where the limit $a \to 0$ has already been taken in the second term as it does not need the regulator. Here the first term is the infinite self-energy of two charges in the limit $a \to 0$ [cf. (58)] and the second term is the Coulomb energy of the two charges a distance $r$ apart.

Similarly, the regulated transverse part is

$$\mathcal{E}^{\perp}_{\mathbf{P},a} = \left(\frac{e^2}{8\pi^3\epsilon_0}\right)r^t r^s\int \chi_a^2(k)(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})_{ts}\frac{1-\cos(\mathbf{k}\cdot\mathbf{r})}{(\mathbf{k}\cdot\mathbf{r})^2}d^3\mathbf{k}. \tag{63}$$

The angular integrations are again straightforward, with the result that

$$\mathcal{E}^{\perp}_{\mathbf{P}} = \frac{e^2}{2\pi^2\epsilon_0}\lim_{a\to 0}\int_0^\infty \chi_a^2(k) \times\left((kr)\mathrm{Si}(kr) + \frac{\sin(kr)}{kr} + \cos(kr) - 2\right)dk, \tag{64}$$

where

$$\mathrm{Si}(t) = \int_0^t \frac{\sin(s)}{s}ds \tag{65}$$

is the usual sine integral. It is convenient to define a quantity $\mathsf{Y}$, which will be discussed further below,

$$\mathsf{Y}_a(r) = \int_0^\infty \chi_a^2(k)(kr)\mathrm{Si}(kr)dk. \tag{66}$$

The remaining integrals are

$$\begin{aligned}
\lim_{a\to 0}\int_0^\infty \chi_a^2(k)\frac{\sin(kr)}{kr}dk &= \frac{\pi}{2r},\\
\lim_{a\to 0}\int_0^\infty \chi_a^2(k)\cos(kr)dk &= \pi\delta(r),\\
-2\lim_{a\to 0}\int_0^\infty \chi_a^2(k)dk &= -\frac{\pi}{a}\Big|_{a\to 0},
\end{aligned} \tag{67}$$

and so in the point-particle limit $a \to 0$,

$$\mathcal{E}_{\mathbf{P}}^{\perp} = \frac{e^2}{4\pi\epsilon_0}\left(2\pi\mathsf{Y}_a(r)|_{a\to 0} + \frac{1}{r} + 2\delta(r) - \frac{2}{a}\Big|_{a\to 0}\right). \tag{68}$$

The second term in (68) is a Coulomb energy; notice it is precisely equal, and of opposite sign, to the second term in (62). The third term is a contact interaction, while the last term is a self-interaction energy, again infinite in the limit. Adding (62) and (68), we finally obtain the full energy for the primitive type 1 case (41) as

$$\mathcal{E}_{\mathbf{P}} = \frac{e^2}{4\pi\epsilon_0}\left(2\pi\mathsf{Y}_a(r)|_{a\to 0} + 2\delta(r) - \frac{1}{a}\Big|_{a\to 0}\right), \tag{69}$$

which is notable because (a) the static Coulomb interaction energy of the particles has canceled completely and (b) it is (69) rather than (62) that occurs in the PZW Hamiltonian [(3) with the straight-line path].

For the infinitely thin straight-line integration path ($a = 0$) the function $\mathsf{Y}_0$ has the form

$$\mathsf{Y}_0 \sim \frac{Z_{\mathcal{C}}}{r}, \quad Z_{\mathcal{C}} = \int_0^\infty x\,\mathrm{Si}(x)dx, \tag{70}$$

where $Z_{\mathcal{C}}$ is a divergent coefficient. It is possible to analyze $\mathsf{Y}$ further using a regulator, for example,

$$\chi_a(k) = e^{-ak/\pi}. \tag{71}$$

With an obvious change of variable, we then have

$$\begin{aligned}
\mathsf{Y}_a(r) &= \frac{1}{r}\int_0^\infty x\,\mathrm{Si}(x)e^{-sx}, \quad s = \frac{2a}{\pi r}\\
&= \frac{1}{r}\left[\frac{\arctan\left(\frac{1}{s}\right)}{s^2} + \frac{1}{s(1+s^2)}\right].
\end{aligned} \tag{72}$$

For $s$ near 0 this is

$$\begin{aligned}
\mathsf{Y}_a(r) &\approx \frac{1}{r}\left[\frac{\pi}{2s^2} + O\left(\frac{1}{s}\right) + \cdots\right]\\
&= \frac{\pi^3 r}{8a^2} + O\left(\frac{a}{r^2}\right) + \cdots,
\end{aligned} \tag{73}$$

which shows that for fixed $a > 0$ this is an energy that increases with increasing $r$. This is essentially the result [33] given for a contribution to the electric field energy of two static quarks with equal and opposite charges fixed at $\mathbf{x}_1$ and $\mathbf{x}_2$ for a state involving the Wilson line

$$\exp\left(\frac{ie}{\hbar}\int_{\mathbf{x}_1}^{\mathbf{x}_2} d\mathbf{z}\cdot\mathbf{a}\right) \tag{74}$$

as a phase factor, with $\mathbf{a}$ in an arbitrary gauge [cf. (11)]; an energy rising linearly with separation is taken as the cause of quark confinement. The evaluation of the energy $\mathcal{E}_{\mathbf{P}}$ is discussed further in Sec. VI, where it is shown to be consistent with other results in the high-energy physics literature obtained from quite different considerations. For now we note here that there is no confinement in electrodynamics and (73) can be understood as the result of the unitary transformation rearranging the distribution of the energy between the charges and the field

Type 2 and type 3 contributions to the energy $\mathcal{E}_{\mathbf{P}}$ arise from multiparticle polarization fields; the simplest examples are the cross terms required for the evaluation of $\mathcal{E}_{\mathbf{P}}$ with

$$\begin{aligned}
\mathbf{P}(\mathbf{x}) &= e\int_{\mathbf{x}_1^e}^{\mathbf{x}^N}\delta^3(\mathbf{z}-\mathbf{x})d\mathbf{z} + e\int_{\mathbf{x}_2^e}^{\mathbf{x}^N}\delta^3(\mathbf{z}-\mathbf{x})d\mathbf{z} \quad \text{(type 2)},\\
\mathbf{P}(\mathbf{x}) &= e\int_{\mathbf{x}_1^e}^{\mathbf{x}^N}\delta^3(\mathbf{z}-\mathbf{x})d\mathbf{z} + e\int_{\mathbf{x}_2^e}^{\mathbf{x}^M}\delta^3(\mathbf{z}-\mathbf{x})d\mathbf{z} \quad \text{(type 3)},
\end{aligned} \tag{75}$$

with $N \neq M$. For the general multicharge system all three types of term will arise. For point charges these are contact interaction contributions to the energy since each term in the polarization field has support on its own line of force, and thus the integrand in $\mathcal{E}_{\mathbf{P}}$ is nonzero only at the points where the lines touch (type 2) at $\mathbf{x}^N$ or intersect (type 3). So, for example, the cross terms from (75) yield

$$\mathcal{E}_{\mathbf{P}} \sim \left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2}{|\mathbf{x}^N-\mathbf{x}_1|^2|\mathbf{x}^N-\mathbf{x}_2|^2}\delta^3(0), \tag{76}$$

where the vectors $\mathbf{r}_n$, $n = 1, 2$, are $\mathbf{x}^N - \mathbf{x}_n$, $n = 1, 2$. This again must be regulated as the $\delta^3(0)$ is ill-defined.

## V. THE PZW TRANSFORMATION AND COHERENT STATES IN FOCK SPACE

In their seminal paper Power and Zienau remarked that the transformation (9) could be viewed as a redefinition of the modes of the field that incorporated the atom as a whole as a source [5] but did not analyze the idea further. This can be done by expressing the PZW transformation in terms of generalized coherent states [34]. Since $\Lambda_{\mathbf{P}}$ [Eq. (7)] is a product of charged particle and field variables and is proportional to the charge $e$, the resulting coherent state parameters involve mixtures of particle and field variables and $e$ and only make sense for the interacting system. Using the mode expansion of the Coulomb gauge vector potential and proceeding to the continuum limit in the usual way [28], the transformation operator (6) may be cast in the form of a coherent state displacement operator as

$$\mathsf{U}_{\mathbf{P}} = \exp\left[\sum_\lambda\int[\alpha(\mathbf{k}:\mathbf{P})_\lambda \mathsf{c}(\mathbf{k})_\lambda^\dagger - \alpha(\mathbf{k}:\mathbf{P})_\lambda^*\mathsf{c}(\mathbf{k})_\lambda]d^3\mathbf{k}\right], \tag{77}$$

where for each mode $\mathbf{k}$ and $\lambda$ the coherent state parameter is

$$\alpha(\mathbf{k}:\mathbf{P})_\lambda = -i\sqrt{\frac{1}{2(2\pi)^3\hbar ck\epsilon_0}}\mathbf{P}(\mathbf{k})\cdot\hat{\boldsymbol{\epsilon}}(\mathbf{k})_\lambda. \tag{78}$$

Here $\mathbf{P}(\mathbf{k})$ is the Fourier transform of the electric polarization field evaluated at the wave vector $\mathbf{k}$. Since $\mathsf{U}_\mathbf{P}$ is formally unitary, the resulting coherent state $\Psi_0(\mathbf{P})$,

$$|\Psi_0(\mathbf{P})\rangle = \mathsf{U}_\mathbf{P}|\Psi_0\rangle, \tag{79}$$

is normalized if the Coulomb gauge Fock space vacuum $\Psi_0$ is normalized.

The transformed annihilation and creation operators for the mode $\mathbf{k}$ and $\lambda$ are, respectively,

$$\begin{aligned}\mathsf{C}(\mathbf{k}:\mathbf{P})_\lambda &= \mathsf{c}(\mathbf{k})_\lambda + \alpha(\mathbf{k}:\mathbf{P})_\lambda,\\ \mathsf{C}(\mathbf{k}:\mathbf{P})^\dagger_\lambda &= \mathsf{c}(\mathbf{k})^\dagger_\lambda + \alpha(\mathbf{k}:\mathbf{P})^*_\lambda\end{aligned} \tag{80}$$

and one still has

$$[\mathsf{C}(\mathbf{k}:\mathbf{P})_\lambda, \mathsf{C}(\mathbf{k}':\mathbf{P})^\dagger_{\lambda'}] = \delta_{\lambda,\lambda'}\delta^3(\mathbf{k}-\mathbf{k}'). \tag{81}$$

We can define a new vacuum state $\Psi_0(\mathbf{P})$ by setting

$$\mathsf{C}(\mathbf{k}:\mathbf{P})_\lambda|\Psi_0(\mathbf{P})\rangle = 0\,\forall\,\mathbf{k} \tag{82}$$

to give a new representation of the Fock space for the system. Every state can then be considered to be constructed from the action of some polynomial involving the (new) annihilation and creation operators on the (new) vacuum state $\Psi_0(\mathbf{P})$.

A straightforward generalization from the single-mode case to the continuum limit shows that $|\Psi_0(\mathbf{P})\rangle$ is related to the free-field vacuum $|\Psi_0\rangle$ by

$$\begin{aligned}|\Psi_0(\mathbf{P})\rangle = \exp\left(-\frac{1}{2}\int\sum_{\lambda=1,2}|\alpha(\mathbf{k}:\mathbf{P})_\lambda|^2 d^3\mathbf{k}\right)\\ \times\exp\left(\int\sum_{\lambda=1,2}\alpha(\mathbf{k}:\mathbf{P})_\lambda\mathsf{C}(\mathbf{k}:\mathbf{P})^\dagger_\lambda\right)|\Psi_0\rangle.\end{aligned} \tag{83}$$

For a given electric polarization field $\mathbf{P}(\mathbf{k})$, the number of photons with wave vector $\mathbf{k}$ and polarization $\lambda$ in the coherent state (83) is

$$n[\mathbf{P}(\mathbf{k})] = \langle\Psi_0(\mathbf{P})|\mathsf{c}(\mathbf{k})^\dagger_\lambda\mathsf{c}(\mathbf{k})_\lambda|\Psi_0(\mathbf{P})\rangle = |\alpha(\mathbf{k}:\mathbf{P})_\lambda|^2 \tag{84}$$

and the total number of photons in the state is

$$\overline{N} = \int\sum_{\lambda=1,2}|\alpha(\mathbf{k}:\mathbf{P})_\lambda|^2 d^3\mathbf{k}. \tag{85}$$

The overlap between the old and new vacuum states is

$$\begin{aligned}\langle\Psi_0|\Psi_0(\mathbf{P})\rangle &= \exp\left(-\frac{1}{2}\int\sum_{\lambda=1,2}|\alpha(\mathbf{k}:\mathbf{P})_\lambda|^2 d^3\mathbf{k}\right)\\ &= \exp\left(-\frac{1}{2}\overline{N}\right).\end{aligned} \tag{86}$$

An explicit evaluation of the integral in (86) requires the specification of a polarization field. As a first example consider restricting the polarization field for an atomic/molecular system to the leading terms of its multipole expansion [28],

$$\mathbf{P}(\mathbf{x}) \approx (\mathbf{d} + \mathbf{Q}\cdot\nabla + \cdots)\delta^3(\mathbf{x}-\mathbf{O}), \tag{87}$$

where $\mathbf{O}$ is the center about which the expansion is made. Taking just the dipole term, Eq. (78) becomes

$$\alpha(\mathbf{k}:\mathbf{P})_\lambda = -i\sqrt{\frac{1}{2(2\pi)^3\hbar ck\epsilon_0}}\mathbf{d}\cdot\hat{\boldsymbol{\epsilon}}(\mathbf{k})_\lambda e^{i\mathbf{k}\cdot\mathbf{O}}. \tag{88}$$

The evaluation of (85) is immediate; the sum over the product of two photon polarization vectors is given by [28]

$$\sum_{\lambda=1,2}\hat{\epsilon}(\mathbf{k})_{\lambda i}\hat{\epsilon}(\mathbf{k})_{\lambda j} = \delta_{ij} - \frac{k_i k_j}{k^2} \tag{89}$$

and all that is left is a divergent integral

$$\overline{N} = \frac{2\alpha}{3\pi}|\boldsymbol{\mu}|^2\int_0^\infty k\,dk, \tag{90}$$

where $\alpha$ is the fine-structure constant[3] and $\mathbf{d} = e\boldsymbol{\mu}$. Introducing a regulator into (90) means including a factor $\chi_a^2(k)$ in the integrand (see Sec. IV), and choosing $\chi_a(k) = \exp(-ak/\pi)$ as before yields

$$\overline{N}_a = \alpha\frac{\pi}{6}\frac{|\boldsymbol{\mu}|^2}{a^2}. \tag{91}$$

This result is partly attributable to an inappropriate use of the customary multipole expansion (87), which is only valid for small $|\mathbf{k}|$ [see (45)], while the integral is dominated by large $|\mathbf{k}|$ values.

Now consider the full line integral form for the electric polarization field; without any real loss of generality we can restrict attention to a two-particle system that is overall electrically neutral. The required Fourier transform is given in (44), and choosing $\mathbf{r}$ as the polar axis, we obtain, after carrying out the polarization sum,

$$\frac{1}{2}|\alpha(\mathbf{k})|^2 = \frac{\alpha}{2\pi}\left(\frac{1-\cos^2(\theta)}{\cos^2(\theta)}\right)\frac{\sin^2[kr\cos(\theta)/2]}{k^3}\chi_a^2(k), \tag{92}$$

where we have included the same regulator as for the dipole approximation. The angular integration over $d\Omega(\mathbf{k})$ is straightforward and there remains the dimensionless quantity (with $s = \frac{2a}{\pi r}$)

$$\frac{\alpha}{\pi}\int_0^\infty\frac{e^{-st}}{t}\left[t\,\mathrm{Si}(t) + \frac{\sin(t)}{t} + \cos(t) - 2\right]dt = \frac{\alpha}{\pi}R(s) \tag{93}$$

for the exponent in (86). It is readily verified that

$$R(s) = \left(\frac{1}{s} - s\right)\arctan\left(\frac{1}{s}\right) + 1 + \ln(-s^2) - \ln(-1-s^2); \tag{94}$$

for small $s$, $R(s)$ is dominated by the first term, and so

$$R(s)|_{s\to 0} \sim O\left(\frac{1}{s}\right). \tag{95}$$

Now $s$ is determined by the ratio $a/r$ and so may become small if $a \to 0$, for fixed $r$, or $r \to \infty$, for fixed $a$. So again the mean

[3]The coefficient $\alpha$ on the right-hand side is the fine-structure constant (in conventional notation), not to be confused with (78).

photon number is divergent in the point particle limit

$$\lim_{a\to 0} R(2a/\pi r) = \infty, \quad 0 < r < \infty. \tag{96}$$

Retaining the full line integral form for the polarization field weakens the singularity in $\overline{N}_a$ as compared to the electric dipole approximation form, but does not remove it. Thus, in the limit of an infinitely thin line ($a \to 0$) Eq. (86) vanishes, that is, the two vacuum states are orthogonal. This implies that the Hilbert spaces $\mathcal{H}[c]$ and $\mathcal{H}[C(\alpha)]$ are orthogonal. One has realizations of the canonical commutation relations for the annihilation/creation operators $(\{\mathsf{c}_{\mathbf{k},\lambda}, \mathsf{c}^\dagger_{\mathbf{k},\lambda}\}; \{\mathsf{C}(\mathbf{k} : \mathbf{P})_\lambda, \mathsf{C}(\mathbf{k} : \mathbf{P})^\dagger_\lambda\})$ which are *not* related by unitary transformation; they are said to be *unitary inequivalent* [14,17]. The practical consequence is that in this limit there is no longer a guarantee that a Coulomb gauge theory based on the free-field Fock space and the general Hamiltonian with $\mathbf{P}^\perp \neq 0$ will lead to identical expectation values.

The exponential operator $\mathsf{U}_\mathbf{P}$ is defined by its power series expansion; the expansion is used in the explicit evaluation of (9) and is required for the demonstration that the perturbation theory expansion of the $S$ matrix is independent of the choice of $\mathbf{P}$ [35]. In the point charge limit the expansion is ill-defined as an operator on the free-field Fock space since

$$\langle\Psi_0|\mathsf{I} + \frac{i}{\hbar}\Lambda_\mathbf{P} + \frac{1}{2!}\left(\frac{i}{\hbar}\right)^2 \Lambda^2_\mathbf{P} + \cdots + |\Psi_0\rangle = 1 + 0 + \infty + \cdots. \tag{97}$$

The operator $\Lambda_\mathbf{P}$ may be regulated by insisting that the length parameter $a$ satisfies $a > 0$. Physically one might expect $\lambda_C$, the Compton wavelength of the charge, to be involved since this is the natural quantum-mechanical parameter to ensure nonrelativistic energies. However, one cannot assume $a = \lambda_C$ since $\lambda_C$ is a constant and the limit $a \to 0$ should describe a quantum-mechanical point charge such as an electron (a structureless entity) [16].

## VI. LINES OF FORCE

The electric polarization field $\mathbf{P}(\mathbf{x})$ is a contribution to the electric field $\mathbf{E}(\mathbf{x})$ due to the charges other than the transverse electric field associated with radiation. As we have seen (Sec. III), the line integral form implies that the electric field is concentrated purely on the path $\mathcal{C}$ ending at the charge. However, as noted earlier, $\mathbf{P}$ is not the solution of the Maxwell equation for the electric field of the charges since $\nabla \wedge \mathbf{P} \neq 0$ in general. A possible way of visualizing the situation is to regard the paths as *lines of force*; this is essentially the view of Faraday [36], who used them to describe the properties of the electromagnetic field. The lines were endowed with physical characteristics, for example, tension and mass, and could move with both transverse and longitudinal oscillations. In this way he aimed to account for the effects of the field on charged bodies and for the propagation of electromagnetic radiation without recourse to an ether. Open lines have equal and opposite charges at their end points, while closed lines describe some state of the field.

The vector $\mathbf{g}$ [Eq. (27)] occurs in a manifestly gauge-invariant formulation of quantum electrodynamics [37];[4] Dirac considered the example of a single electron located at a point $\mathbf{X}$ and examined the electric field around it. At a point $\mathbf{x}$ in space this turns out to exceed the electric field of the vacuum state by an amount $e\epsilon_0^{-1}\mathbf{g}(\mathbf{x} : \mathbf{X})$. The choice of $\mathbf{g}$ specified in (28) leads to the result that the excess field is precisely the Coulomb field of the charge, whereas a more general choice such as (29) leads to the Coulomb field *plus* a field of pure electromagnetic radiation as the excess.

Dirac interpreted the electric field associated with the path $\mathcal{C}$ as a single Faraday line of force between the charge and the reference point $\mathbf{O}$, which he took to be spatial infinity. He also noted that a closed path would describe a state of the electromagnetic field that is in some way connected with the particles because the elementary charge $e$ occurs in the coefficient of the integral. He further conjectured that a novel quantum electrodynamics might be constructed using the lines of force (the paths $\mathcal{C}$) as the basic dynamical variables from which our conventional notions of charged particles and electromagnetic fields would be derived. However, as here, Dirac regarded the paths as fixed classical objects and got no further than associating a phase factor $e^{i\phi}$,

$$\phi \sim \frac{1}{\hbar}\int d^3\mathbf{x}\,\mathbf{P}(\mathbf{x})\cdot\mathbf{a}(\mathbf{x}) = \frac{e}{\hbar}\int_\mathcal{C}^\mathbf{X} \mathbf{a}(\mathbf{z})\cdot d\mathbf{z}, \tag{98}$$

with the particle annihilation/creation operators (the obvious generalization to a relativistic theory uses the 4-potential $\mathsf{a}_\mu$ and paths in space-time). That approach was subsequently developed in detail (see, for example, [38,39]). The PZW representation described here can be seen as a nonrelativistic implementation of the above ideas.

Looking to the future, this suggests a novel interpretation of the polarization fields appearing in the PZW representation in which the paths themselves could be considered as dynamical variables. Since we must include the time, the path variable $\mathbf{z} = \mathbf{z}(\sigma, t)$ must be thought of as a field with one space dimension (the path parameter $\sigma$) and the time $t$. There is a caveat however; because there is no unique assignment of a path to a physical situation the paths have to be regarded as unphysical working variables, very much like the role played by the field potentials. Thus one has to ensure that physical observables are independent of any specific choice of path in the same way as one insists on gauge invariance in the conventional exposition of Maxwell's theory. The natural way to do that is to consider all possible paths in a suitably weighted average.

The idea of superposition of paths leads naturally to an approach that uses path integral techniques. Instead of having to choose a specific classical path, physical quantities could be expressed as functional integrals over the path variable with an appropriately defined measure, i.e., as an average over all possible paths with a suitable weighting. Thus the expectation value in a specified state of any functional $\Gamma$ of the paths $\{\mathcal{C}\}$

[4]The quantity $c_r(x, x')$ in Dirac's equations (18), (19), and (40) is essentially $\mathbf{g}$.

would be given by the functional integral

$$\langle \Gamma \rangle = \frac{1}{Z} \int \mathcal{D}\mathbf{z}\, \Gamma \rho(\mathbf{z}), \tag{99}$$

where $Z$ is a normalization constant such that $\langle 1 \rangle = 1$, and $\rho(\mathbf{z})$ is the density matrix for the state (not to be confused with the charge density). A QED formalism based on line integrals and the resulting contact interactions that maintains Lorentz invariance as in the usual theory has been constructed [26,40,41]. It is not known what implications that might have for the PZW formulation of nonrelativistic QED discussed here. This is an avenue for future work; one interesting approach is based on a return to its Lagrangian formulation.

The classical Lagrangian that leads to the Hamiltonian (3) can be built out of the quantities in (22); first the standard Lagrangian for an electromagnetic field is given by

$$L_{\rm rad} = -\frac{1}{4}\epsilon_0 c^2 \int f_{\mu\nu} f^{\mu\nu} d^3\mathbf{x} = \frac{1}{2}\epsilon_0 \int (\mathbf{E}\cdot\mathbf{E} - c^2 \mathbf{B}\cdot\mathbf{B}) d^3\mathbf{x}. \tag{100}$$

Similarly, the interaction term is simply [24]

$$L_{\rm int} = -\frac{1}{2}\int p_{\mu\nu} f^{\mu\nu} d^3\mathbf{x} = \int \mathbf{P}\cdot\mathbf{E}\, d^3\mathbf{x} + \int \mathbf{M}\cdot\mathbf{B}\, d^3\mathbf{x}. \tag{101}$$

The Lagrangian is completed by the addition of the nonrelativistic formula for the kinetic energy of the charges; it is related to the usual nonrelativistic Schwarzschild Lagrangian in an arbitrary gauge by a total time derivative and so yields the same equations of motion. From this point of view, the Coulomb gauge formalism has no distinguished place in relation to (3).

Now one can make the same construction as (100) using the displacement field $d_{\mu\nu}$ [Eq. (22)] in place of the free-field field tensor $f_{\mu\nu}$ so we might consider another Lagrangian

$$L_{\rm dis} = -\frac{1}{4}\epsilon_0 \int d_{\mu\nu} d^{\mu\nu} d^3\mathbf{x}. \tag{102}$$

This Lagrangian, when simplified using (22), yields (100) and (101), and an additional term arising purely from the polarization tensor

$$\begin{aligned} L_{\rm pol} &= -\frac{\mu_0}{4}\int p_{\mu\nu} p^{\mu\nu} d^3\mathbf{x} \\ &= \frac{1}{2\epsilon_0}\int \mathbf{P}\cdot\mathbf{P}\, d^3\mathbf{x} - \frac{\mu_0}{2}\int \mathbf{M}\cdot\mathbf{M}\, d^3\mathbf{x}. \end{aligned} \tag{103}$$

The first term in (103) is precisely the last term in (3), while the second term is novel and has not previously been considered. This additional term (103) is *not* a total time derivative and so will yield altered Lagrangian equations of motion and a modified Hamiltonian. Terms in the Lagrangian that depend on only particle positions contribute unchanged to the Hamiltonian with a simple change of sign, so one sees that the first term in (103) will cancel precisely with the last term in (3). The square of the magnetization however involves velocities and so will contribute to the definition of the canonical momenta. This approach confirms the calculation in Sec. IV as may be seen as follows.

The action integral associated with (103),

$$S_{\rm pol} = \int L_{\rm pol} d^3\mathbf{x}\, dt, \tag{104}$$

has recently been studied using the relativistic form (47) for $p^{\mu\nu}$ and shown to be highly singular; we omit the details of the calculation and simply quote the result that (104) can be transformed to the form [26,40]

$$S_{\rm pol} = -\frac{e^2}{2\epsilon_0}\delta^2(0) S_{\rm NG} + \text{a contact interaction term} + \cdots, \tag{105}$$

where $S_{\rm NG}$ is the Nambu-Goto action for a relativistic string [31] and $\delta^2(0)$ is the singular spatial delta function in two dimensions evaluated at the origin. The leading term of the nonrelativistic limit of (105) is just [42]

$$S_{\rm pol}^{\rm NR} \sim= \frac{e^2}{2\epsilon_0}\delta^2(0)\int dl\, dt, \tag{106}$$

where $l$ is the arc length along the line of force; for the straight-line path between the two charges this is simply $r$. Here $\delta^2(0)$ is an inverse area, so (105) and (106) lead to the same conclusion as the discussion in Sec. IV about the energy $\mathcal{E}_{\mathbf{P}}$ since the nonrelativistic limit of (104) is obtained directly from (103).

## VII. CONCLUSION

The general Hamiltonian for the nonrelativistic QED of atoms and molecules is formulated in terms of polarization fields and the field strengths. The polarization fields can be expressed in terms of line integrals over paths joining the positions of pairs of charges; a given path however does not correspond to any specified physical situation, and the arbitrariness in the paths replaces the freedom to make gauge transformations in the formulation based on the field potentials. The paths may be interpreted as lines of force; in essentially all applications a fixed classical path, the straight line joining the pair of charges, is implied. A natural generalization in a quantum theory is to consider paths that fluctuate (quantum paths), which is an idea still to be explored; however that may be, the calculation of physical observables must not depend on the paths since they do not correspond to a definite physical situation.

The use of an electric polarization field with a nonzero transverse component implies that energy is shared between the field and the lines of force in a way that is different from the sharp separation seen in the usual Coulomb gauge Hamiltonian. For point charges the polarization fields are distributions that give rise to singular interactions which need to be regularized. Comparison of (62) and (64) shows that the cancellation of the Coulomb terms is *independent* of the choice of the regulator function $\chi_a(k)$. We remark that these calculations are based on a straight-line path $\mathcal{C}$ in the integrations; the longitudinal contribution is obviously path independent. It is hard to see how this cancellation of the static Coulombic energy between the longitudinal and transverse contributions to the energy could be avoided by a choice of some other path. This can be seen in the PZW transformation viewed as a coherent state displacement and in the energy calculations in Sec. IV. Clearly, an energy like (73) has no physical significance in electrodynamics;[5] it must be remembered that the physical quantity is the full Hamiltonian, which gives the

[5]Formulas (69) and (70) together are a correction to the earlier result [Eq. (33)] given in [32] (see also [43]).

expected equations of motion whatever electric polarization field is assumed. This requires that the charge-field interaction terms in (3) must be involved in removing the singular terms revealed by these evaluations of $\mathcal{E}_{\mathbf{P}}$. So far this has only been achieved partially in the framework of perturbation theory.

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