Connections Between the Thermodynamics of Classical Electrodynamic Systems and Quantum Mechanical Systems for Quasielectrostatic Operations

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The thermodynamic behavior is analyzed of a single classical charged particle in thermal equilibrium with classical electromagnetic thermal radiation, while electrostatically bound by a fixed charge distribution of opposite sign. A quasistatic displacement of this system in an applied electrostatic potential is investigated. Treating the system nonrelativistically, the change in internal energy, the work done, and the change in caloric entropy are all shown to be expressible in terms of averages involving the distribution of the position coordinates alone. A convenient representation for the probability distribution is shown to be the ensemble average of the absolute square value of an expansion over the eigenstates of a Schrödinger-like equation, since the heat flow is shown to vanish for each hypothetical "state." Subject to key assumptions highlighted here, the demand that the entropy be a function of state results in statistical averages in agreement with the form in quantum statistical mechanics. Examining the very low and very high temperature situations yields Planck's and Boltzmann's constants. The blackbody radiation spectrum is then deduced. From the viewpoint of the theory explored here, the method in quantum statistical mechanics of statistically counting the "states" at thermal equilibrium by using the energy eigenvalue structure, is simply a convenient counting scheme, rather than actually representing averages involving physically discrete energy states.

1. INTRODUCTION

The theory of stochastic electrodynamics (SED), or classical electrodynamics with the assumption *not* imposed that classical electromagnetic thermal radiation must vanish at $T = 0$, has had a number of successes at explaining

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supposedly purely quantum mechanical behavior. This purely classical physical theory attempts to consistently address the equilibrium between charges and radiation. References 1–5 review this work.[2] The basis of SED is conceptually fairly simple: classical electromagnetic fields and classical charged particles obey Maxwell's equations and the relativistic generalization of Newton's second law of motion (e.g., the Lorentz–Dirac equation for point charges). Upon considering Earnshaw's theorem,[7, 8] the only possible means for classical electromagnetic radiation and classical charged particles to be in equilibrium with each other is when fluctuating fields and motion are present. Thus, "stable" atomic systems, if describable from within classical electrodynamics, must consist of rapid fluctuating motion of electrons and nuclei, while radiating and picking up energy from the fluctuating radiation that must also be present to result in statistical equilibrium. The enormous mass difference between the electrons and nuclei would result in the approximate fluctuation amplitude of the nuclei being substantially less than the electrons, so that the electrons follow essentially orbiting-jiggling motion about the nuclei.

Despite some success, so far SED has largely only predicted the correct quantum behavior for linear systems, where the equations of motion can be solved in detail. For nonlinear systems, perturbation methods employed to date have not yielded correct agreement with physical observation.[9, 10] [3] However, questions still exist on the correct mathematical methods to be employed when solving the difficult, nonlinear stochastic partial differential equations of motion for realistic electrodynamic systems in nature.[10, 11] [4]

The present article builds on earlier work on the basic thermodynamic behavior we should expect for electrodynamic systems.[5, 8, 12–17] In this earlier work, the only systems analyzed in full detail were linear ones: specifically, the nonrelativistic charged harmonic oscillator[5, 8, 12, 14] and blackbody radiation enclosed by conducting walls.[13] Reference 5 discussed qualitatively how this analysis may carry over to more general nonlinear systems, while Refs. 15–17 analyzed certain thermodynamic aspects for general electrodynamic systems interacting with thermal radiation. Here, some of these issues for general nonlinear systems are explored more quantitatively.

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[2] Reference 2 provides a very extensive review and list of references on SED. Reference 6 is a book review on this text. Reference 4 is a semi-popular review on aspects of SED.

[3] In particular, see the articles listed in Ref. 9. Additional references are cited in Ref. 10.

[4] A few misprints need to be corrected in Ref. 10: (i) in the dimensionless equations of (25) and (30), $\hbar$ should not be present, as was given correctly earlier in Eq. (22); (ii) in Eq. (25) a factor of 1/2 is needed in the fourth line down; and (iii) z should be replaced by z'' in the fifth line down in Eq. (25).

However, unlike the earlier work on linear systems, here we are still limited in mathematical techniques for fully addressing nonlinear systems. Nevertheless, some progress can be made by analyzing the key physical points for linear systems, and then examining how these points must carry over to nonlinear systems, if SED is to apply to systems found in nature. The physical assumptions introduced will be cleared stated, so that future research efforts can probe and test them more deeply.

Consequently, in Sec. 2 a very simple system will be analyzed that can be calculated in detail using the present methods of SED. Certain key approximations satisfied by this system will be identified and argued to hold for more complicated systems. Section 3 then examines single particle systems in nonlinear electrostatic binding potentials. One particularly important example included in this category is the hydrogen atom. Section 4 turns to examine the hypothetical case where the particle's position is described by a probability distribution that would arise from an eigenstate of a Schrödinger-like equation. Although the unphysical nature of excited states representing statistical equilibrium states is noted, insight is gained into the significance of these states by showing that no heat is radiated during quasistatic displacement operations *if* such a state can be approximately satisfied for a finite period of time. This proof is carried out by considering the change in internal energy and the work done due to quasistatic displacements of the atomic system within an applied electrostatic potential.

Section 5 turns to the more physically realistic case of thermal equilibrium. The probability distribution for the position of the charged particle is expressed in terms of the absolute square value of an expansion over the complete set of eigenfunctions of an equation of the form of Schrödinger's time independent wave equation. A key assumption is introduced regarding the expectation value, or ensemble average, of the coefficients of the eigenfunctions. The change in entropy is then found using the formulae in Sec. 3 for the change in internal energy and the work done during quasistatic displacements. Demanding that the entropy must be a function of state then results in the same functional form for statistical averages that is prescribed in quantum statistical mechanics.

Section 6 next examines the very low and very high temperature regimes and deduces Planck's and Boltzmann's constants by comparing the present results with what is found in nature. Section 7 contains concluding remarks.

Despite the apparent equivalence between the results obtained here and the predictions of quantum statistical mechanics, an entirely different physical basis exists in the two approaches. The analysis here involves a classical charged particle with a continuous range of energies that is in thermal equilibrium with classical electromagnetic thermal radiation. The

viewpoint explored here is that the fundamental microscopic laws of classical electrodynamics mentioned at the beginning of this section may be perfectly satisfactory for describing the regime of atomic physics, and may represent a more fundamental physical understanding and description of nature than does quantum mechanics.[5] In contrast, the ideas of traditional classical statistical mechanics appear to be flawed and need to be revised when dealing with classical charged particles in thermal equilibrium with classical electromagnetic radiation. The three laws of thermodynamics are fine. To illustrate these points, Refs. 8 and 12–14 showed how the laws of thermodynamics (first, second, and third laws) can consistently hold for simple classical electrodynamic systems, while still having classical fluctuating motion and fields present at $T = 0$ and while *not* imposing the assumptions of traditional classical statistical mechanics. References 15–18 contain related discussions.

Much remains to be done before we can accept SED as a fully realistic physical theory of nature, since the equations of motion have not been solved in detail for realistic nonlinear systems, the existence of equilibrium between radiation and charged particles has not been proven, plus a host of other problems exist. In spite of this, the aim of the present article is to shed detailed insight into the likely thermodynamics of classical charged systems *if* this equilibrium should indeed exist. *If so*, then the agreement shown here between (1) ensemble averages of classical systems and (2) quantum mechanical statistical averages involving weighted sums over energy eigenvalues, could be understood as the latter being simply a convenient summation scheme, rather than a sum over populations of systems in discrete energy levels. More specifically, the counting of "states" in quantum statistical mechanics could then be understood as a masked means of accounting statistically, via the means shown here, for what is really happening physically. The concluding comments in Sec. 7 emphasizes this point by recalling very similar statements made by E. Schrödinger in his lectures on statistical mechanics.[19]

2. SED TEST CASE: ELECTROSTATIC DISPLACEMENT OF LINEAR OSCILLATOR

Let us again consider the displacement operations in Ref. 8, but let us pick an even simpler system to analyze. The purpose here is to make as

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[5] Attention here is restricted to only the atomic domain of physics. However, possibly the other regimes of physics may also be treatable using the main principles of SED, as briefly discussed in Sec. I in Ref. 5. A key point of SED that should be important here is that equilibrium between classical particles and *all* classical fields must be taken into account at thermal equilibrium.
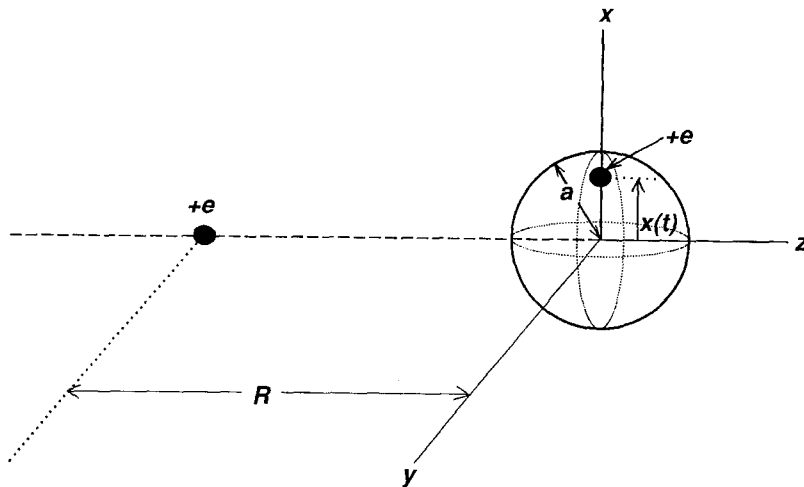
Fig. 1. Sketch of fluctuating electric dipole model interacting with a fixed $+e$ charge. The $-e$ uniform spherical charge gives rise to a simple harmonic-oscillator potential acting on the $+e$ charge, which here is assumed to be constrained to motion only along the x axis. Far from the $-e$ spherical charge and the $+e$ fluctuating charge, their combined electromagnetic field is that of a fluctuating electric dipole.

close a connection as possible with the single-particle Schrödinger equation. Hence, only *one* oscillating charge is considered here. The terms that are typically dropped in SED resonant calculations will be carefully noted. We will again consider the simplified model of an atom, described in Ref. 8, consisting of a fluctuating electric dipole that obeys a linearized form of the Lorentz–Dirac equation of motion that would arise from a spinless, charged point particle oscillating in a simple harmonic-oscillator (SHO) potential. Figure 1 illustrates one simple means of picturing this electric dipole system, where far from its center the system exhibits the electromagnetic fields of a fluctuating electric dipole. Here, a $+e$ charge, with mass m, oscillates inside a $-e$ uniform spherical charge distribution of radius a. Let us assume that oscillations are constrained to occur only along the x axis.[6] The dipole oscillator will be slowly displaced along the z axis with respect to the fixed (i.e., nonoscillating) charge $+e$ in Fig. 1. The distance R will be assumed to be much larger than a, while a will be assumed to be much larger than the average amplitude of oscillation.

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[6] This constraint can most certainly be relaxed; as can readily be verified, the same physical results shown here will occur if oscillations in three dimensions are allowed. To emphasize the physics, however, for this section we will concentrate on the one-dimensional oscillator.

Following the reasoning in Ref. 8, Sec. III, the equations of motion will be:

$$m\ddot{x} = -m\omega_0^2 x + eE_{f,x} + m\Gamma\frac{d^3x}{dt^3} + eE_{in,x}(0, t) \tag{1}$$

where (1) $\mathbf{E}_f$ is the electric field of the fixed $+e$ charge, (2) the x component of $\mathbf{E}_f$ is $E_{f,x} = ex/(x^2 + R^2)^{3/2} \approx ex/R^3$, (3) $\omega_0^2 = e^2/(ma^3)$, (4) $\mathbf{E}_{in}(\mathbf{x}, t)$ is the incident electric field of the thermal radiation, and (5) $\Gamma \equiv 2e^2/3mc^3$.

Assuming the steady-state solution to be given by the Fourier transform solution, then

$$x(t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} d\omega\, e^{-i\omega t}\tilde{x}(\omega) \tag{2}$$

$$\tilde{x}(\omega) = \frac{(e/m)\,\tilde{E}_{in,x}(0, \omega)}{(-\omega^2 + \omega_r^2 - i\Gamma\omega^3)} \tag{3}$$

$$\omega_r^2 \equiv \omega_0^2 - \frac{e^2}{mR^3} \tag{4}$$

Upon slowly displacing the fixed $+e$ charge, heat, $\langle\mathcal{Q}\rangle$, in the form of electromagnetic thermal energy, will flow into some large volume $\mathcal{V}$ enclosing the dipole oscillator and fixed charge, according to

$$\langle\mathcal{Q}\rangle = \langle\Delta\mathcal{U}_{int}\rangle - \langle\mathcal{W}\rangle \tag{5}$$

Here $\langle\Delta\mathcal{U}_{int}\rangle$ represents the expectation value of the change in internal energy $\mathcal{U}_{int}$ within $\mathcal{V}$, while $\langle\mathcal{W}\rangle$ represents the expectation value of the work done *on* the system during the displacement. (See Ref. 5 for a detailed description of these terms, including $\mathcal{Q}$, where $\mathcal{Q}$ is expressed in terms of Poynting's vector for radiation flow.) Here, general changes in quantities will be denoted by Δ, while δ will be used to represent infinitesimal changes.

Calculating $\langle\Delta\mathcal{U}_{int}\rangle$ first,

$$\mathcal{U}_{int} = m^*\gamma c^2 + \frac{1}{8\pi}\int_{\mathcal{V}} d^3x(\mathbf{E}_{tot}^2 + \mathbf{B}_{tot}^2) \tag{6}$$

where m^* is the bare mass of the oscillating charge, and $\mathbf{E}_{tot}$ and $\mathbf{B}_{tot}$ represent the total electromagnetic fields due to the dipole oscillator, the fixed charge, and the thermal radiation fields. Following the mass renormalization described in Refs. 5 and 8, assuming that changes in the internal

energy are largely due to the nonrelativistic velocity regime of the energy distribution, and dropping the Schott energy term, the mc^2 term, and the surface term in Eq. (20) of Ref. 8, we obtain that the terms that will make a nonnegligible contribution to $\langle \Delta \mathscr{U}_{int} \rangle$ are

$$\mathscr{U}'_{int} = \frac{m\dot{x}^2}{2} + \frac{m\omega_0^2 x^2}{2}$$

$$+ \frac{1}{8\pi} \int_{\mathscr{V}} d^3x \left[\begin{array}{c} (\mathbf{E}^2_{osc\text{-}a} + \mathbf{B}^2_{osc\text{-}a}) + 2(\mathbf{E}_f \cdot \mathbf{E}_{in}) + 2(\mathbf{E}_{osc} \cdot \mathbf{E}_f) \\ + 2(\mathbf{E}_{osc} \cdot \mathbf{E}_{in} + \mathbf{B}_{osc} \cdot \mathbf{B}_{in}) + (\mathbf{E}_{in} \cdot \mathbf{E}_{in} + \mathbf{B}_{in} \cdot \mathbf{B}_{in}) \end{array} \right]$$

$$\tag{7}$$

The first term is the nonrelativistic kinetic energy after renormalization, while the second equals the electrostatic potential energy due to the cross-term electromagnetic energy between the $+e$-oscillating and $-e$-spherical charges. The first term in the volume integral equals the electromagnetic energy of the acceleration fields of the $+e$ oscillating charge, where "osc-a" denotes the acceleration fields. Reference 8 can be used to evaluate this term, as well as the two previous energy terms. As for the next term involving $\mathbf{E}_f \cdot \mathbf{E}_{in}$, its expectation value will be zero since $\langle \mathbf{E}_f(\mathbf{x}) \cdot \mathbf{E}_{in}(\mathbf{x}, t) \rangle = \mathbf{E}_f(\mathbf{x}) \cdot \langle \mathbf{E}_{in}(\mathbf{x}, t) \rangle = 0$. We need to evaluate the next term involving $\mathbf{E}_{osc} \cdot \mathbf{E}_f$, where $\mathbf{E}_{osc}$ is the total electric field of the dipole oscillator. As for the "osc-in" term, again we can use Ref. 8 to obtain its average. Finally, for the "in-in" term, its average will not change unless we change the temperature of the radiation.[12]

Thus, all of the above terms, including the kinetic and potential energies, can be deduced from the analysis in Ref. 8, except for

$$\frac{2}{8\pi} \int_{\mathscr{V}} d^3x \, \mathbf{E}_{osc} \cdot \mathbf{E}_f = -\frac{e^2}{R} + \frac{e^2}{(R^2 + x^2)^{1/2}} \approx -\frac{e^2}{2R^3} x^2 \tag{8}$$

We will make use of Eqs. (49) and (50) in Ref. 8, where now $C(\omega) = -\omega^2 + \omega_r^2 - i\omega^3 \Gamma$, $N = 1$ [the last term in Eq. (37) is absent here], the indices i and j take on only the value 1, and $M_{Ai; Bj}$ trivially equals one for $A = B = 1$ and $i = j = 1$. By applying the resonant approximation,[7] we obtain for the expectation value of, respectively, (1) the sum of Eq. (8)

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[7] This approximation has been described many times elsewhere. See, for example, pp. 569 and 570 in Ref. 20 or pp. 1653 and 1654 in Ref. 21.

plus the second term in Eq. (7), and (2) the first term in Eq. (7), the following:

$$\frac{m}{2}\left(\omega_0^2 - \frac{e^2}{mR^3}\right)\langle x^2\rangle = \pi\omega_r^2 \int_0^\infty d\omega \, h_{\text{in}}^2(\omega)\frac{1}{\omega}\,\text{Im}\left(\frac{1}{C(\omega)}\right) \approx \frac{\pi^2 h_{\text{in}}^2(\omega_r)}{2} \qquad (9)$$

$$\frac{m}{2}\langle\dot{x}^2\rangle = \pi\int_0^\infty d\omega \, h_{\text{in}}^2(\omega)\,\omega\,\text{Im}\left(\frac{1}{C(\omega)}\right) \approx \frac{\pi^2 h_{\text{in}}^2(\omega_r)}{2} \qquad (10)$$

The "potential energy" term in Eq. (9) arises entirely from the "electrostatic-Coulombic" energy of interaction between the three charges in Fig. 1.

As for the remaining electromagnetic energy terms in Eq. (7), from Eqs. (51) and (53) in Ref. 8, with $N = 1$ and $i = j = 1$,

$$U_{\text{EM}\,|\,\text{in}} \equiv \frac{1}{8\pi}\int_{\mathscr{V}} d^3x[\langle \mathbf{E}_{\text{osc-a}}^2 + \mathbf{B}_{\text{osc-a}}^2\rangle + 2\langle \mathbf{E}_{\text{osc}}\cdot\mathbf{E}_{\text{in}} + \mathbf{B}_{\text{osc}}\cdot\mathbf{B}_{\text{in}}\rangle]$$

$$\approx \pi\int_0^\infty d\omega \, h_{\text{in}}^2(\omega)\,\text{Im}\left(\frac{2i\Gamma\omega^2}{C(\omega)}\right) \qquad (11)$$

Making the usual resonance approximation, changes in this energy term is taken to be negligible compared to changes in the other terms.

Thus, our important contributions to the internal energy arise entirely from the resonant approximation of the electrostatic energy of interaction between the three charges and the kinetic energy [i.e., Eqs. (9) and (10), respectively]. Changes in the remaining terms are small in comparison and will be neglected in subsequent analysis. For strong connections to exist between SED and QED, these remaining terms must represent the perturbation terms in QED due to vacuum fluctuations. (Similar conclusions were deduced for the much more complicated system in Ref. 14, which analyzed a system with many dipole oscillators and no externally applied fields, in contrast to the analysis here of a single oscillating charge under the influence of the applied field of the $+e$ charge.)

Turning now to the work done in slowly displacing the dipole oscillator (or, equivalently, the $+e$ fixed charge), as in Sec. V of Ref. 8, we need to evaluate the expectation value of the Lorentz force that needs to be opposed to displace the system. As was true with the energy terms, where we found that radiation terms could be neglected, here one can show that in the resonance approximation the average Lorentz force due to the thermal radiation fields is negligible in comparison with the average electrostatic

force. We assume that R is sufficiently small that the unretarded van der Waals condition of $\omega_r R/c \ll 1$ applies. One obtains

$$\langle F_{\text{Lor}, z}(t) \rangle \approx \left\langle -\frac{e^2}{R^2} + \frac{e^2 R}{(R^2 + x^2)^{3/2}} \right\rangle \approx -\frac{3e^3}{2R^4} \langle x^2 \rangle$$

$$\approx -\frac{3e^2}{2mR^4\omega_r^2} \cdot \pi^2 h_{\text{in}}^2(\omega_r) = -\frac{\partial \omega_r}{\partial R} \cdot \frac{\pi^2 h_{\text{in}}^2(\omega_r)}{\omega_r} \tag{12}$$

Since the externally applied force required to quasistatically displace the dipole oscillator must be equal to the negative of the above, then $\langle \mathscr{W} \rangle = -\langle F_{\text{Lor}, z} \rangle \, \delta R$ for a small displacement δR.

From Eqs. (5), (9), (10), and (12) we obtain that the heat flow into a large volume $\mathscr{V}$ surrounding this system will be given by

$$\langle \mathscr{Q} \rangle = \delta[\pi^2 h^2(\omega_r)] - \delta R \frac{\partial \omega_r}{\partial R} \frac{\pi^2 h_{\text{in}}^2(\omega_r)}{\omega_r}$$

$$= \delta R \pi^2 \frac{\partial \omega_r}{\partial R} \left[\frac{\partial h_{\text{in}}^2(\omega_r)}{\partial \omega_r} - \frac{h_{\text{in}}^2(\omega_r)}{\omega_r} \right] + \delta T \frac{\partial}{\partial T} (\pi^2 h^2(\omega_r)) \tag{13}$$

due to an infinitesimal displacement δR, and as accompanied by an infinitesimal change in temperature δT. From this equation, changes in caloric entropy can be calculated via $\delta S_{\text{cal}} = \langle \mathscr{Q} \rangle / T$. Moreover, we see that our now familiar result from the analysis of other systems[8, 12, 13] also holds here. More specifically, during a reversible isothermal ($\delta T = 0$) displacement operation, only one spectrum will satisfy the condition that no heat flows: namely,

$$\frac{\partial h_{\text{in}}^2(\omega)}{\partial \omega} = \frac{h_{\text{in}}^2(\omega)}{\omega} \tag{14}$$

for $\omega = \omega_r$. This result should hold for different values of a and R, and therefore for different values of ω_0 and ω_r in Eq. (4). Consequently, at $T = 0$, $h_{\text{in}}^2 = \kappa\omega$, which yields the spectral form for classical electromagnetic zero-point (ZP) radiation of $\rho_{\text{ZP}}(\omega) = \omega^2 h_{\text{ZP}}^2/c^3 = \kappa\omega^3/c^3$. The best numerical value of κ to agree with experiment can then be found by experimentally measuring, for example, the average force in Eq. (12).

3. GENERALIZATION: ELECTROSTATIC DISPLACEMENT OF SED NONLINEAR SYSTEM

We will now generalize the above results to address the quasistatic displacement of electrodynamic systems that obey a nonlinear equation of

motion. Due to the present undeveloped set of mathematical techniques needed to address this problem in detail, in contrast to the linear problem just discussed, we will proceed by making some assumptions, guided by our previous analysis. In keeping with the previous section, a key assumption will be that the contribution of the incident radiation electromagnetic fields to the *changes* entailed by $\langle \Delta \mathscr{U}_{int} \rangle$ and $\langle \mathscr{W} \rangle$ enters as small perturbation terms that should correspond to the vacuum fluctuation terms in QED. Thus, here we will deal only with the electrostatic energy of interaction and the electrostatic force.

Let the system of interest consist of a single point charge $-e$ at position $\mathbf{R} + \mathbf{z}(t)$ that moves under the influence of an electrostatic binding potential energy $-e\phi_b(\mathbf{z}(t))$ due to a positive fixed charge distribution $\rho_b(\mathbf{x})$ with net charge $+Ze$. Let $\mathbf{R}$ denote the approximate center of ρ_b. When this charge distribution consists of a point charge with $Z = 1$, then our system is equivalent to the usual classical model for the hydrogen atom. For other charge distributions, such as a spherical uniform charge distribution, or a spherical distribution dependent on radius, then linear and nonlinear oscillator potentials can be formed, respectively, at least within the charge distribution. Outside the charge distribution, the potential is equivalent to an ionized atom with atomic number Z.

Let $\phi_a(\mathbf{x})$ be an externally applied electrostatic potential to our system. In the quasistatic operation described here, we will displace our atomic system within ϕ_a by slowly displacing the binding charge distribution ρ_b, while keeping the shape of ρ_b fixed; i.e., $\mathbf{R} \to \mathbf{R} + \Delta\mathbf{R}$. Alternatively, the following problem could be phrased in terms of keeping the position of the atom fixed, while slowly changing $\phi_a(\mathbf{x})$. In terms of investigating this problem in detail, the electrostatic binding potential ϕ_b is what makes the analysis quite difficult due to the nonlinearity that it introduces to the equation of motion for the $-e$ charge. As for ϕ_a, typically this potential varies much more slowly in space for real atomic systems and can usually be treated by linearizing it over the region of the atom.

As for the kinetic energy of the $-e$ point charge, let us assume that the *change* in this energy arises largely from the change in the non-relativistic regime of the particle's distribution of velocities, as occurred in the case analyzed in Sec. 2.[8] Consequently, the average internal energy

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[8] Here, $P(\mathbf{x} \mid \mathbf{x} = \mathbf{z}(t)) \, d^3x$ represents the probability of the random variable $\mathbf{z}(t)$, at time t, falling within the infinitesimal volume d^3x at the point $\mathbf{x}$. We only consider the situation of a stationary distribution in time here; i.e., we do not consider $P(\mathbf{x}, t \mid \mathbf{x} = \mathbf{z}(t))$. From the standpoint of an ensemble, then $\mathbf{z}(t)$ would be indexed with the parameter θ, and the randomness associated with $\mathbf{z}(t)$ would be due to the variations of $\mathbf{z}(t)$ as θ is varied. Alternatively, assuming ergodicity, then θ could be fixed and the same probability distribution would arise as t is varied. For simplicity, $P(\mathbf{x} \mid \mathbf{x} = \mathbf{z}(t))$ will often be written as $P(\mathbf{x})$ here.

that we will be interested in here is [compare with Eqs. (6) and (7)]

$$\langle \mathscr{U}_{int} \rangle = \left\langle \mathscr{U}_{-e,\,int} + \int_{\mathscr{V}} d^3x'\,\rho_b(x')\,\phi_a(\mathbf{R}+x') + \mathscr{U}_{EM,\,in} \right\rangle \qquad (15)$$

where

$$\langle \mathscr{U}_{-e,\,int} \rangle = \left\langle \frac{m\,|\dot{\mathbf{z}}|^2}{2} + V(\mathbf{R}, \mathbf{z}) \right\rangle \qquad (16)$$

is the average of the internal energy of the $-e$ charge due to its non-relativistic kinetic energy and the electrostatic potential energy

$$V(\mathbf{R}, \mathbf{x}) = -e\phi_b(\mathbf{x}) - e\phi_a(\mathbf{R}+\mathbf{x}) \qquad (17)$$

and $\langle \mathscr{U}_{EM,\,in} \rangle \equiv U_{EM,\,in}$ is the expectation value of the last term in Eq. (7) due to the energy of the incident radiation in a large volume $\mathscr{V}$ enclosing the classical atom. For the case of thermal equilibrium, changes in $U_{EM,\,in}$ will only arise when the temperature changes. Consequently, in the present article $U_{EM,\,in}$ will play only a minor role since no physical work will be done to change its value, in contrast to the situation in Ref. 13 involving the displacement of conducting plates. Reference 12 analyzed $U_{EM,\,in}$ in detail for the thermal situation of interest here involving a large volume $\mathscr{V}$. As for final comments on the above, the second term in Eq. (15) is not stochastic in nature and can be pulled outside of the ensemble average. To evaluate $\langle \mathscr{U}_{-e,\,int} \rangle$, we will make use of a generalization to the classical virial theorem, to which we now turn.

The Lorentz–Dirac equation can be expressed by $d\mathbf{p}/dt = \mathbf{F}$, where $\mathbf{p} = m\gamma\dot{\mathbf{z}}$ and $\mathbf{F}$ is the sum of forces, including the effective one due to radiation reaction [see Eq. (4) in Ref. 10]. Since we are assuming that we are dealing with a stochastic process that is stationary in time when ρ_b is held fixed, then $\langle d/dt(\mathbf{z} \cdot \mathbf{p}) \rangle = 0$ yields

$$\langle \dot{\mathbf{z}} \cdot \mathbf{p} \rangle = -\langle \mathbf{z} \cdot \mathbf{F} \rangle \qquad (18)$$

The above result is exact. Now comes our approximations. We will assume that changes in either the left of right side of Eq. (18), due to either changes in temperature or quasistatic displacements, is largely due to the nonrelativistic contribution in the above. Hence, let us approximate changes is $\langle \dot{\mathbf{z}} \cdot \mathbf{p} \rangle$ by changes in $m\langle |\dot{\mathbf{z}}|^2 \rangle$. Also, let us assume that the radiation reaction and the rapidly varying incident radiation force both contribute negligibly to changes in $\langle \mathbf{z} \cdot \mathbf{F} \rangle$. Without actually solving the nonlinear stochastic differential equation of motion, we cannot rigorously

justify these approximations. Consequently, these approximations remain assumptions for the present analysis. Perhaps the best justifications that can be offered here are (1) these approximations are correct for the linear harmonic oscillator just analyzed, and (2) a similar result holds in non-relativistic quantum mechanics.[9] Indeed, as another partial justification, if the nonrelativistic radiation reaction of $m\Gamma(d^3z/dt^3)$ is used, then one can show that $\langle z \cdot m\Gamma(d^3z/dt^3) \rangle = 0$ under equilibrium conditions for any system. Retaining the full relativistic radiation reaction force does not appear, in general, to yield zero for this average; however, in keeping with our nonrelativistic approximation for the average kinetic energy, we can expect that this extra contribution is negligible in comparison with the following term. We obtain:

$$\Delta\langle m\,|\dot{z}|^2 \rangle \approx \Delta\langle z \cdot (-e\,\nabla\phi_b|_z - e\,\nabla\phi_a|_{R+z}) \rangle \tag{19}$$

so that

$$\Delta\langle \mathscr{U}_{-e,\,\text{int}} \rangle \approx \Delta\left\langle \frac{z \cdot \nabla_z V}{2} + V(R, z) \right\rangle \tag{20}$$

Thus, at this lowest level of approximation, to evaluate changes in this internal energy we only need to deal with the probability density distribution $P(x\,|\,x = z(t))$,[8] rather than also needing to consider the distribution for $\dot{z}$. This result is fortunate, since one difficult aspect about calculating $\Delta\langle \mathscr{U}_{\text{int}} \rangle$ is in dealing with the joint probability distribution for z and $\dot{z}$. In quantum mechanics this problem does not arise, partly because in wave mechanics the nonrelativistic momentum $m\dot{z}$ is replaced by an operator $(\hbar/i)\,\nabla$ that acts on $\Psi(x, t)$. We accomplished a somewhat similar result here by only examining the average of $|\dot{z}|^2$ and by the use of the virial theorem for classical systems.

Turning to the work $\langle \mathscr{W} \rangle = -\langle F_{\text{Lor}} \rangle \cdot \delta R$ that is done when displacing the atomic system by a small amount δR, we will again compute $\langle F_{\text{Lor}} \rangle$ by assuming that the main contribution is due to the average of the electrostatic force in our problem:

$$\langle \mathscr{W} \rangle = \left[\langle -e\,\nabla\phi_a|_{R+z} \rangle + \int_{\mathscr{V}} d^3x'\, \rho_b(x')\, \nabla\phi_a|_{R+x'} \right] \cdot \delta R \tag{21}$$

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[9] More precisely, from Eq. (24) follows the quantum mechanical virial theorem that $2\langle u_i|\,T_{\text{op}}\,|u_i \rangle = \langle u_i|\,z \cdot \nabla V\,|u_i \rangle$, where $T_{\text{op}} = -\hbar^2\nabla^2/2m$, for an energy eigenstate $u_i(z)$ of Schrödinger's equation, as discussed in Ref. 22, p. = 180. For a thermal equilibrium situation, which is primarily our focus here, the quantum mechanical prescription is to average the above with the factor $e^{-E_i/kT}/\sum_j e^{-E_j/kT}$.

Work due to the second term above, which involves only the work on the nonfluctuating $+e$ binding charge due to ϕ_a, equals the corresponding change in the electrostatic potential energy represented by the second term in Eq. (15).

Consequently, Eqs. (5), (15), (20), and (21) yield

$$\langle \mathcal{Q} \rangle \approx \delta \langle \tfrac{1}{2} \mathbf{z} \cdot \nabla_z V + V \rangle - \langle \delta \mathbf{R} \cdot \nabla_{\mathbf{R}} V \rangle \tag{22}$$

for a small displacement $\delta \mathbf{R}$. For the moment only isothermal conditions are considered, so that $\delta T = 0$ and, therefore, $\delta U_{\mathrm{EM, in}} = 0$. Thus, at this lowest level of approximation, to evaluate this heat flow, we again only need to concern ourselves with $P(\mathbf{x})$.

The above result agrees with our earlier result in Sec. 2 for the specific case of an electric dipole SHO. To see this, one simply needs to substitute in $V = \tfrac{1}{2} m \omega_0^2 x^2 + e^2 / \sqrt{R^2 + x^2} \approx \tfrac{1}{2} m \omega_r^2 x^2 + e^2 / R$ into Eq. (22), then use Eqs. (4) and (9) to yield Eq. (13) for the isothermal condition of $\delta T = 0$.

4. HYPOTHETICAL CASE: PROBABILITY DISTRIBUTION DUE TO SCHRÖDINGER EIGENFUNCTION

Let us now examine a particular "what if" situation (the much more realistic situation of thermodynamic equilibrium will be discussed in Sec. 5): namely, what if $P(\mathbf{x}) = |u_i(\mathbf{x})|^2$, where u_i is the ith eigenstate, with eigenvalue E_i, of the equation

$$-\mathscr{A} \nabla^2 u + Vu = Eu \tag{23}$$

The results we will obtain hold for arbitrary nonzero values of $\mathscr{A}$. Without a doubt, however, the main interest here will be when $\mathscr{A} = \hbar^2 / 2m$, so as to correspond to a time-independent eigenstate of Schrödinger's equation, and thereby agree with situations observed in experimentation.

Proponents of SED may at first object to this *ad hoc* introduction of quantum phenomena into classical physics. For example, except for the ground state, none of the eigenstates of Schrödinger's equation can be viewed as being stationary in time within SED. Instead, at $T = 0$, all "excited states" must decay to the ground state, due to, loosely speaking, spontaneous emission induced by the classical electromagnetic ZP field. As a partial consequence of this observation, plus for other reasons, Schrödinger's eigenstates should not be viewed as physical states within the framework of SED.[23, 24]

Of course, within QED, this viewpoint also more or less holds, although the language is somewhat different. Eigenstates of Schrödinger's

equation are actually only approximately physically realizable for finite
lengths of time, since the radiative corrections that are typically treated as
perturbations in quantum mechanics, change the physical status of these
states. In contrast, in SED these radiative effects are automatically
included. Consequently, separating the effects to observe whether the same
physical predictions are being described by the two theories is, at least to
date, quite difficult.

Consequently, for now we only examine what happens if $P(\mathbf{x}) = |u_i(\mathbf{x})|^2$. The point here will be to deduce the physical consequences if this
condition is approximately met for some period of time, during which the
electrostatic field ϕ_a is slowly varied, thereby slowly changing E_i in
Eq. (23). Certainly, at the very least, this examination should be of great
interest for the ground state. In addition, this analysis also sheds some
insight into the physical meaning of a system approximating a quantum
mechanical excited state for a finite period of time.

For any second-differentiable function $f(\mathbf{x})$, and for any value of $\mathscr{A}$,
one can show that the following identity holds:

$$\mathbf{x} \cdot (\nabla_{\mathbf{x}} V) f = -2\mathscr{A}\nabla^2 f + [\mathbf{x} \cdot \nabla_{\mathbf{x}}, (-\mathscr{A}\nabla^2 + V)]_- f \qquad (24)$$

where $[A, B]_- \equiv AB - BA$ for operators A and B. The above result is used
in deriving the quantum virial theorem, where $\mathscr{A}$ is assigned the value
$\hbar^2/(2m)$.[9, (22)]

From Eqs. (20), (23), and (24),

$$\langle \mathscr{U}_{-e, \text{int}} \rangle = \int d^3x\, u_i^*(\mathbf{x}) \left\{ -\mathscr{A}\nabla^2 + \tfrac{1}{2}[\mathbf{x} \cdot \nabla, [-\mathscr{A}\nabla^2 + V(\mathbf{R}, \mathbf{x})]]_- \right.$$
$$\left. + V(\mathbf{R}, \mathbf{x}) \right\} u_i(\mathbf{x})$$
$$= \int d^3x\, u_i^*(\mathbf{x})[-\mathscr{A}\nabla^2 + V(\mathbf{R}, \mathbf{x})]\, u_i(\mathbf{x}) = E_i \qquad (25)$$

Here, ∇^2 was assumed to be Hermitian when operating on u_i, which is
equivalent to assuming that u_i vanishes sufficiently fast at infinity that
surface terms can be ignored when integrating by parts. Thus, assuming the
classical virial theorem to hold, and assuming $P(\mathbf{x}) = |u_i(\mathbf{x})|^2$, then the
above *average* internal energy is just the eigenvalue of Eq. (23).

Noting that $\delta \mathbf{R} \cdot \nabla_{\mathbf{R}} V = \delta V = \delta H_{\text{op}}$, where H_{op} is the operator
$-\mathscr{A}\nabla^2 + V(\mathbf{R}, \mathbf{x})$, then Eq. (22) yields

$$\langle \mathscr{Q} \rangle_{P(\mathbf{x}) = |u_i|^2} = \delta E_i - \int d^3x\, u_i^*(\mathbf{x})(\delta H_{\text{op}})\, u_i(\mathbf{x}) = 0 \qquad (26)$$

due to the Hellman–Feynman theorem.[25] This result expresses a relationship between δE_i and the perturbation δH_{op} of the electrostatic potential energy that is quite familiar to physicists from first order perturbation theory in quantum theory. However, our interest in Eq. (26) goes much deeper. We obtain the very interesting result that *if* the classical probability density $P(\mathbf{x} \mid \mathbf{x} = \mathbf{z}(t))$ is equal to the square of the magnitude of an eigenfunction of Eq. (23), then no heat will flow out of some large volume surrounding the bound particle system upon making a small displacement δR within the electrostatic potential ϕ_a.[10]

The above result is related to the following results in conventional nonrelativistic quantum mechanics. If, for example, an electron is in an eigenstate u_i of Eq. (23), where $\mathscr{A} = \hbar^2/(2m)$, then it does not radiate. Upon making a quasistatic change in an applied electrostatic potential, the electron will essentially remain in the same eigenstate of Eq. (23), where V is slowly changed. This result holds in quantum mechanics both for small and large changes in V (see, for example, Ref. 26).

Of course, as mentioned earlier, in QED no quantum state, except the ground state, can actually exist forever (at $T = 0$) without changing to another state. Likewise, some excited states chosen from quantum mechanics may, *at best*, be only approximately physically realizable for finite periods of time in SED. In particular, the excited states of a harmonic oscillator are not physical states in SED, as was described quite clearly in Ref. 24.

Nevertheless, the above result is significant in the following way: *Not just any probability function $P(\mathbf{x})$ will yield, $\langle \mathscr{Q} \rangle = 0$, for a classical single-particle, bound charged system, upon a quasistatic change in applied electric field. Rather, $P(\mathbf{x})$ must change its functional form in a precisely defined way.* Under our nonrelativistic, dipole approximations, we see that one possibility for this defined manner is when $P(\mathbf{x}) = |u_i(\mathbf{x})|^2$ and u_i satisfies the Schrödinger-like equation of Eq. (23).

In addition, one could construct a large class of hypothetical probability distributions that also yield no heat flow by writing $P(\mathbf{x}) = \sum_i C_i |u_i(\mathbf{x})|^2$, where C_i are constant coefficients. The linearity of Eq. (22) in terms of $P(\mathbf{x})$ will yield a zero heat flow for any such function, which may at first make one doubt about the significance of the above results. Nevertheless, two critically important restrictions apply here. The first, and by far the weakest one, is that this representation of $P(\mathbf{x})$ will not allow just *any* probability density function to yield zero heat flow, as $P(\mathbf{x})$ must

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[10] More specifically, no heat will flow, as demonstrated to the lowest order of approximation shown here; however, this should be a general result at $T = 0$ to all orders of approximation. This result of no radiation heat flow can be cast in terms of electromagnetic radiation as expressed by Poynting's vector. See the analysis leading up to Eq. (30) in Ref. 5.

change in the precisely defined way mentioned above during the quasistatic displacement. Specifically, upon making a noninfinitesimal displacement ΔR, then $P(\mathbf{x}) = \sum_i C_i |u_i(\mathbf{x})|^2$, with C_i fixed, must change according to how the eigenfunctions $u_i(\mathbf{x})$ change in Eq. (23) due to $\mathbf{R} \to \mathbf{R} + \Delta \mathbf{R}$ and, therefore, $V(\mathbf{R}, \mathbf{x}) \to V(\mathbf{R} + \Delta \mathbf{R}, \mathbf{x})$ in Eqs. (17) and (23). Thus, although one could think of a fairly arbitrary initial function $P_{\mathrm{I}}(\mathbf{x})$, except for $P_{\mathrm{I}}(\mathbf{x}) \geqslant 0$ $\forall \mathbf{x}$, and $\int d^3 x\, P(\mathbf{x}) = 1$, and perhaps find a set of C_i coefficients that enable one to express $P_{\mathrm{I}}(\mathbf{x})$ as $\sum_i C_i |u_i(\mathbf{x})|^2$, the initial function $P_{\mathrm{I}}(\mathbf{x})$ may have only a slight resemblance to the final function $P_{\mathrm{II}}(\mathbf{x})$ after the displacement in a strong, spatially varying electrostatic field.

The second restriction, and by far the strongest one, is that our results apply to near equilibrium situations. Selecting any arbitrary $P(\mathbf{x}) = \sum_i C_i |u_i(\mathbf{x})|^2$ will of course not satisfy this restriction in general. In particular, only under stationary stochastic conditions can the classical virial theorem be deduced, is its starting point was that $(d/dt)\langle \mathbf{z} \cdot \mathbf{p} \rangle = 0$. This condition must hold prior to the quasistatic displacement, as well as afterwards, since this result is used to deduce the internal energy at these times, or, rather, the difference in the internal energy between these times. Moreover, the quasistatic approximation, which assumes near equilibrium conditions hold, was used in calculating the work done during the displacement. (See Sec. V in Ref. 8 and Sec. IX in Ref. 12.)

If we look for essentially exact situations where these conditions hold, such as where $\langle (d/dt)(\mathbf{z} \cdot \mathbf{p}) \rangle = 0$ for all of time before and after the quasistatic (not necessarily infinitesimal) displacement, then there is only one situation we should consider: thermal equilibrium conditions, which is the topic we turn to next. Otherwise, our result of no heat flow is only approximately valid during the finite time that the system is in a metastable state, such as might be approximately represented by some quantum mechanical excited states with long decay times.

By the conclusion of this article, it will be seen that even the restriction to thermal equilibrium conditions is not sufficiently tight when considering the question of what physical states actually yield no heat flow during quasistatic displacements. As anticipated in Sec. 2 and in earlier work,[8, 13, 14] but as deduced more generally here, there is only *one* thermal equilibrium situation where no heat will flow: the temperature $T = 0$ equilibrium state. We will later discuss the significance of Eq. (23) for describing this state, and on choosing the appropriate value of $\mathscr{A}$.

5. THERMODYNAMIC EQUILIBRIUM

We now consider a means for describing thermodynamic equilibrium conditions. Some of the reasoning will appear quite familiar, as it somewhat

parallels the reasoning in quantum mechanics. However, key differences will also be noted, as we will demand that classical physics is obeyed.

Let $P_T(\mathbf{x})$ be the probability density associated with the single, bound charged particle discussed in the previous section, when the particle is in thermal equilibrium at temperature T with thermal radiation. To ensure that $P_T(\mathbf{x})$ is positive definite, let $P_T(\mathbf{x})$ equal the ensemble average of $|\Psi_{[\theta]}(\mathbf{x}, t)|^2$, where $\Psi_{[\theta]}(\mathbf{x}, t)$ is a complex function such that $|\Psi_{[\theta]}(\mathbf{x}, t)|^2$ specifies at time t the probability density of finding the particle at position $\mathbf{x}$ for a subensemble, indicated by $[\theta]$, of the entire ensemble of particles. Hence,

$$P_T(\mathbf{x}) \equiv \langle |\Psi_{[\theta]}(\mathbf{x}, t)|^2 \rangle \tag{27}$$

where the average is over all subensembles. Thermal equilibrium implies this average is independent of t.

We next expand $\Psi_{[\theta]}(\mathbf{x}, t)$ in terms of the complete set of eigenfunctions of Eq. (23):

$$\Psi_{[\theta]}(\mathbf{x}, t) = \sum_i c_{[\theta], i}(t)\, u_i(\mathbf{x}) \tag{28}$$

where $u_i(\mathbf{x})$ will be assumed to be normalized such that $\int d^3x\, |u_i(\mathbf{x})|^2 = 1$, over the confining space of interest.[11]

The above steps should be perfectly general, while the next one is where key, critical assumptions are made, namely, that

$$\langle c^*_{[\theta], i}(t)\, c_{[\theta], j}(t) \rangle = \delta_{ij} A_i(E_0, E_1, E_2,...; T) \tag{29}$$

Two main assumptions are contained in this relationship. First, the δ_{ij} factor indicates we are assuming that the coefficients $c_{[\theta], i}(t)$ are uncorrelated for $i \neq j$. A similar assumption is usually made in SED involving the coefficients of the Fourier expansion of the thermal relation fields. However, in that case there are strong reasons for requiring this condition, since,

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[11] Only a sum over discrete eigenvalues is indicated in Eq. (28), as would be appropriate if the particle was localized to a finite region of space by the binding potential. Strictly speaking, this restriction is not really appropriate for thermal equilibrium conditions, since some atoms will certainly be ionized at any nonzero temperature. This consideration brings in the question of whether the atom is contained in a box or not. If so, then the binding potential is no longer due to only $\rho_b(\mathbf{x})$ of the classical atomic system, but must also take into account the walls of the retaining box. At the most fundamental level this consideration complicates the problem enormously, since now the problem involves all the atoms in the walls, which in turn have electrons with fluctuating trajectories about nuclei. At the more phenomenological level, we can treat $V(\mathbf{R}, \mathbf{x})$ in Eq. (17) as though it increases sharply to infinity for points near the walls of the container.

roughly speaking, a time average of two Fourier terms will yield zero if the terms are not the same. In the present case, there are less obvious reasons for making such an assumption. The physical correctness of the δ_{ij} factor in Eq. (29) undoubtedly depends on how the subensembles are chosen when writing Eq. (28). Moreover, the chosen value of $\mathscr{A}$ in Eq. (23), to be discussed in Sec. 6, will have a bearing on the choice of subensembles, and undoubtedly also on the physical accuracy of the above assumption.

Second, the factor $A_i(E_0, E_1, E_2,...; T)$ indicates the coefficient of the ith eigenfunction is assumed to statistically depend upon all the energy eigenvalues of Eq. (23), as well as the temperature. We note that related and similar assumptions are made in the development of quantum statistical mechanics [i.e., see Sec. 84 and Eqs. (78.4) and (83.23) in Ref. 27]. However, despite the analogy with quantum statistical mechanics, the above relation of Eq. (29) is intended to include motions of particles following *classical* trajectories in space. A deeper probing of Eq. (29) would be quite desirable in future research. At this point one can only say that at the very least there is nothing obviously nonclassical about the above step.

Let us now examine some consequences of imposing the condition of Eq. (28), by paralleling the analysis of Refs. 12 and 13, which was carried out for much more specific systems. Our aim here will be to calculate the internal energy, the caloric entropy, and the work done, and then demand that the entropy be a function of state. First, from Eqs. (20), (27)–(29), (24), and (25),

$$\langle \mathscr{U}_{-e,\,\text{int}} \rangle = \sum_i A_i E_i + C \tag{30}$$

where C is a constant and the sum is over all eigenvalues of Eq. (23). We note that without the imposition of the δ_{ij} factor in Eq. (29), the internal energy of Eq. (30) would contain an additional term of

$$U'_{\text{int}} = \langle c^*_{[\theta],\,j}(t)\, c_{[\theta],\,i}(t) \rangle (E_i - E_j) \int d^3 x\, u_j^*(\mathbf{x})\, \frac{(\mathbf{x} \cdot \mathbf{V})}{2}\, u_i(\mathbf{x}) \tag{31}$$

which does not in general equal zero.

Using the above to find the caloric entropy,

$$\delta S_{\text{cal}} = \frac{1}{T} \left(\delta T\, \frac{\partial \langle \mathscr{U}_{\text{int}} \rangle}{\partial T} + \delta \mathbf{R} \cdot \nabla_{\mathbf{R}} \langle \mathscr{U}_{\text{int}} \rangle - \langle \mathscr{W} \rangle \right)$$

$$= \frac{1}{T} \left[\delta T \left(\frac{\partial \langle \mathscr{U}_{-e,\,\text{int}} \rangle}{\partial T} + \frac{\partial U_{\text{EM,\,in}}}{\partial T} \right) + \delta \mathbf{R} \cdot \left(\nabla_{\mathbf{R}} \langle \mathscr{U}_{-e,\,\text{int}} \rangle + \langle e \nabla \phi_{\text{a}} \rangle \right) \right]$$

$$= \frac{\delta T}{T} \left(\sum_i \frac{\partial A_i}{\partial T} E_i + \frac{\partial U_{\text{EM, in}}}{\partial T} \right) + \frac{1}{T} \delta \mathbf{R} \cdot \sum_i (\nabla_{\mathbf{R}} A_i) E_i$$

$$+ \frac{1}{T} \delta \mathbf{R} \cdot \sum_i A_i \left(\nabla_{\mathbf{R}} E_i + \int d^3x \, |u_i(\mathbf{x})|^2 \, e \nabla \phi_a|_{(\mathbf{x} + \mathbf{R})} \right) \tag{32}$$

From Eqs. (17) and (26), the term in parenthesis in the last summation above, equals zero. Consequently,

$$\delta S_{\text{cal}} = \frac{1}{T} \left(\sum_i E_i \, \delta A_i + \delta U_{\text{EM, in}} \right) \tag{33}$$

The indicated change in A_i is due to the total change involving (1) $T \to T + \delta T$ and (2) $\mathbf{R} \to \mathbf{R} + \delta \mathbf{R}$, the latter of which affects each eigenvalue E_i of Eq. (23) via the amount δE_i in Eq. (26). The change in $U_{\text{EM, in}}$ is due to the heat that flows into the volume $\mathscr{V}$ upon changing the temperature of the thermal radiation by δT.

Similarly, one can show that the work done on the $-e$ charge when the binding charge is quasistatically displaced by $\delta \mathbf{R}$, equals

$$\langle \mathscr{W}_{-e} \rangle = \delta \langle \mathscr{U}_{-e, \text{int}} \rangle + \delta U_{\text{EM, in}} - T \delta S_{\text{cal}} = \sum_i A_i \, \delta E_i \tag{34}$$

where $\langle \mathscr{W}_{-e} \rangle$ equals the first term in Eq. (21).

Demanding that S_{cal} be a function of state of T and R, and therefore equating expressions for $\partial^2 S_{\text{cal}} / \partial T \, \partial R_s$ in Eq. (32), yields

$$\sum_i \left(T \frac{\partial A_i}{\partial T} \frac{\partial E_i}{\partial R_s} + \frac{\partial A_i}{\partial R_s} E_i \right) = 0 \tag{35}$$

where R_s, with $s = 1, 2, 3$, indicates the three Cartesian coordinates of R. Making the substitution of $\varepsilon_i = E_i / T$, and following similar steps to Ref. 12, Sec. IV.B, results in

$$T \sum_i \left[T \frac{\partial A_i}{\partial T} \bigg|_{\varepsilon} \frac{\partial \varepsilon_i}{\partial R_s} + \sum_j \frac{\partial A_i}{\partial \varepsilon_j} \bigg|_{T, \varepsilon | j} \left(-\varepsilon_j \frac{\partial \varepsilon_i}{\partial R_s} + \varepsilon_i \frac{\partial \varepsilon_j}{\partial R_s} \right) \right] = 0 \tag{36}$$

where $|_\varepsilon$ indicates that ε_k, for all k, are held fixed, and $|_{T, \varepsilon | j}$ indicates that T and ε_k, for all $k \neq j$, are held fixed. Hence, one way to satisfy Eq. (36),

regardless of the value of **R**, and therefore of ε_i and $\nabla_{\mathbf{R}}\varepsilon_i$, and regardless of the value of T, is when

$$\frac{\partial A_i}{\partial \varepsilon_j}\bigg|_{T,\,\varepsilon\,|\,j} = \frac{\partial A_j}{\partial \varepsilon_i}\bigg|_{T,\,\varepsilon\,|\,i} \qquad (37)$$

$$\frac{\partial A_i}{\partial T}\bigg|_{\varepsilon} = 0 \qquad (38)$$

If the main assumption of Eq. (29) is accepted, then the above results are quite general. We saw how the Schrödinger wave *representation* yields that the last term in Eq. (32) equals zero, which was related to no heat flowing in a hypothetical pure Schrödinger wave state. We also saw how Eqs. (30), (33), and (34) bear a strong resemblance to the corresponding predictions of quantum statistical mechanics. This *resemblance* arose despite the fact that we are *not* counting physical states with discrete energy levels. Nevertheless, the internal energy, caloric entropy, and work done can be expressed in sums over energy eigenvalues of the complete set of Schrödinger wave functions that were used to express the probability density of finding the particle. The resemblance between the classical and quantum predictions is fairly close; this connection will now be made even tighter.

Regarding Eq. (29), a natural expectation is that the correlation function of the coefficients of the ith labelled Schrödinger energy eigenfunction should depend most strongly on the ith energy eigenvalue, and only weakly, if at all, on the other eigenvalues. However, some dependence of A_i on E_j for $j \neq i$ *is* required, since from Eqs. (27)–(29),

$$1 = \int d^3x\, P_T(\mathbf{x}) = \sum_i A_i(E_0, E_1, E_2,...;\, T) \qquad (39)$$

The simplest functional form of A_i to ensure the above normalization, yet yield a strong dependence on E_i, as well as satisfy Eq. (38), is:

$$A_i(E_0, E_1, E_2,...;\, T) = \frac{a(\varepsilon_i)}{a(\varepsilon_0) + a(\varepsilon_1) + \cdots + a(\varepsilon_n) + \cdots} \qquad (40)$$

To satisfy Eq. (37), requires that

$$\frac{\partial a(\varepsilon_i)}{\partial \varepsilon_i}\frac{1}{a(\varepsilon_i)} = \frac{\partial a(\varepsilon_j)}{\partial \varepsilon_j}\frac{1}{a(\varepsilon_j)}. \qquad (41)$$

Hence, both sides must equal a constant, which will be introduced as $-1/k'$ here. Thus,

$$\frac{a(\varepsilon_i)}{a(\varepsilon_j)} = \frac{\exp(-\varepsilon_i/k')}{\exp(-\varepsilon_j/k')} \tag{42}$$

and

$$A_i(E_0, E_1, E_2,...; T) = \frac{\exp(-(E_i/k'T))}{\sum_i \exp(-(E_j/k'T))} \tag{43}$$

6. TEMPERATURE EXTREMES AND IDENTIFICATION OF CONSTANTS $\mathscr{A}$ AND k'

Let us now turn to look at the very low and very high temperature predictions of our analysis. These extreme conditions will enable us to fix the two parameters in our formulae, namely, $\mathscr{A}$ in Eq. (23) and k' in Eq. (43). First we note that k' in Eqs. (42) and (43) must be positive if the contribution to the average energy in Eq. (30) is to decrease at higher energy eigenvalues and if the lower rather than higher energy eigenvalues are to be the main contributors at low temperature.

The probability density of finding a particle at position x is

$$P_T(\mathbf{x}) = \sum_i |u_i(\mathbf{x})|^2 \exp\left(-\frac{E_i}{k'T}\right)\frac{1}{Z} \tag{44}$$

where

$$Z \equiv \sum_j \exp\left(-\frac{E_j}{k'T}\right) \tag{45}$$

Thus, our analysis predicts that

$$P_{T=0}(\mathbf{x}) = |u_0(\mathbf{x})|^2 \tag{46}$$

In terms of consistency, the above result is quite fortunate, since the $T = 0$ equilibrium state must yield that no heat should flow during quasistatic displacement operations. We already showed in Sec. 4 that if $P(\mathbf{x}) = |u_i(\mathbf{x})|^2$ for any i, then this condition held. (However, we also discussed the strong doubt that a bound classical charged particle could undergo a trajectory that would yield a statistical equilibrium condition with a $|u_i(\mathbf{x})|^2$

probability density for *any* value of i. One only needs to think of the $i \neq 0$ excited state of a charged particle in a harmonic oscillator potential, with the nodes of $P(\mathbf{x}) = 0$, to realize the unlikelihood of this situation. The $i = 0$ eigenfunction of Eq. (23) does not have this problem, at least not for the commonly discussed $\rho_b(\mathbf{x})$ situations.) The $i = 0$ case then yields a satisfactory $T = 0$ equilibrium state, at least according to this criteria.

The result of Eq. (46) is also satisfactory from another standpoint. In recollection of the variational theorem in quantum mechanics, from Eqs. (30) and (39), and assuming $E_0 < E_i$ for $i \neq 0$,

$$\langle \mathcal{U}_{-e,\,\text{int}} \rangle \geqslant \sum_i A_i E_0 = E_0 \tag{47}$$

Since the $i = 0$ eigenvalue, E_0, equals $\langle \mathcal{U}_{-e,\,\text{int}} \rangle$ at $T = 0$ [Eqs. (30) and (43) with $C = 0$], then this internal energy at $T = 0$ is the lowest possible average energy for the $-e$ charge at any temperature T, as one might naturally expect. More precisely, E_0 is the lowest energy eigenvalue for the particular value of the parameter $\mathcal{A}$ chosen in Eq. (23), which leads to the next point.

Exploring the $T \approx 0$ situation further, enables us to ignore k' and focus just on $\mathcal{A}$. Several options are available for deducing the best value of $\mathcal{A}$ to yield as close agreement as possible with physical observation. For example, experimental measurements at $T \approx 0$ of

$$\langle \mathbf{F}_{\text{Lor}} \rangle = -e \int d^3 x \, |u_0(\mathbf{x})|^2 \, \nabla \phi_a(\mathbf{x} + \mathbf{R}) \tag{48}$$

in Eq. (21) would enable one to deduce $\mathcal{A}$. Alternatively, to yield agreement between (1) the SED analysis in Sec. 2 on a charged particle in a SHO potential, (2) the above analysis in Secs. 3, 4, and 5 for a charged particle in an electrostatic binding potential, and (3) the usual connection between quantum mechanics and SED for a SHO,[23] yields that

$$\mathcal{A} = \frac{\hbar^2}{2m} \tag{49}$$

is the proper connection. In light of Eq. $=$ (49), the measurement of Eq. (48) then yields an experimental means of measuring $\hbar$, given e and m. A similar procedure was discussed in Ref. 13, Sec. V.B, of deducing $\hbar$ by measuring the Casimir force between conducting plates. Essentially what one is doing here is deducing the scaling factor of the radiation spectrum at $T = 0$ that agrees with experimental observation.

Now we turn to deduce k'. The high temperature regime is useful here. For a one-dimensional SHO as in Sec. 2, then from Eqs. (23) and (49), with $\phi_a = 0$ and $V = -e\phi_b = \frac{1}{2}m\omega_o^2 x^2$, and from Eqs. (30) and (43) with $C = 0$ in Eq. (30), one obtains that

$$\langle \mathscr{U}_{-e,\, \text{int}} \rangle = \frac{1}{2} \hbar\omega_0 \coth\left(\frac{\hbar\omega_0}{2k'T}\right) \underset{\hbar\omega_0 \ll k'T}{=} k'T \tag{50}$$

Hence, $k' = k_B$, where k_B is Boltzmann's constant. Comparisons with other systems can also be made. The high temperature regime enables the easy identification of k_B.

Finally, the use of (1) Eqs. (9) and (10), with $R \to \infty$, (2) the first part of Eq. (50), and (3) Eq. (16) in Ref. 12, yields that the *classical* blackbody radiation spectrum is given by

$$\rho_{\text{in}}(\omega, T) = \frac{\omega^2}{c^3} h_{\text{in}}^2(\omega, T) = \frac{\hbar\omega^3}{2\pi^2 c^3} \coth\left(\frac{\hbar\omega}{2k_B T}\right) \tag{51}$$

which agrees with the generalized Wien's displacement law of Eq. (27) in Ref. 12.[12]

7. CONCLUDING REMARKS

The main accomplishments here have been the deduction of (1) the statistical averages for the change in internal energy, the work done, and the change in caloric entropy for quasistatic displacements within an electrostatic potential of a single charged particle classical atomic system, (2) the probability density distribution of position for this system at thermal equilibrium [Eq. (44)], and (3) the blackbody radiation spectrum for classical electromagnetic radiation. From these quantities other thermodynamic functions can also be readily calculated, such as changes in the Helmholtz free energy, the Gibbs free energy, and enthalpy. Averages at thermal equilibrium of any quantities involving only position, such as $\langle |\mathbf{x}|^2 \rangle$, can also be found.

The key points used to obtain the above results for this particular system are: (1) the recognition, from the linear example in Sec. 2, that the nonrelativistic kinetic energy and the electrostatic potential energy are the

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[12] Other researchers in SED, as well as much earlier researchers, have made extensive investigations into the classical blackbody radiation spectrum. Much of this work, in particular by Boyer, Marshall, and others, is summarized in Ref. 2. In particular, see Chap. 5.

main terms to retain when calculating changes in the internal energy, and the electrostatic Lorentz force is the main term to retain when calculating the work done; (2) the imposition of the classical virial theorem and establishing that the change in average internal energy, the work done, and the change in caloric entropy can all be expressed in terms of the probability distribution for the position of the charged particle; (3) noting that the heat flow equals zero for the particle in a hypothetical quantum mechanical state, thereby simplifying the expression for the change in the classical caloric entropy [Eq. (32)]; (4) demanding that the caloric entropy be a function of state, and (5) requiring that no heat will flow during quasistatic displacements at $T = 0$. The last two points were also found to be important in Refs. 8, 12, and 13, where the zero-point radiation spectrum and the generalized Wien displacement law were deduced upon analyzing the thermodynamics of two very different linear electrodynamic systems.

The results reported here are critically dependant on the main assumption of Eq. (29), and to a lesser extent on Eq. (40). Although the assumptions seem to be reasonable ones, their importance needs to be emphasized so that future work by researchers may help to more deeply probe the validity, or invalidity, of these assumptions.

If the thermal equilibrium between classical charges and electromagnetic radiation can be proven to hold, which to date has *not* been the case,[9-11] [3] then the classical statistical averages deduced here of *continuous* energy levels, shows how the quantum mechanical eigenvalue scheme enables the average to *appear* as averages over discrete energy levels. A particularly illuminating monograph on quantum statistical mechanics that strongly expresses a very similar view on the eigenvalue scheme of energies is Ref. 19 by Schrödinger. Below are some of Schrödinger's relevant comments[13]:

"The view that a physical process consists of continual jump-like transfers of energy parcels between microsystems cannot, when given serious thought, pass for anything but a sometimes convenient metaphor. To ascribe to every system always one of its sharp energy values is an indefensible attitude. ... The thermodynamical functions depend on the quantum mechanical level-schemes, not on the gratuitous allegation that these levels are the only allowed states."

"... the permutation numbers and the statistical entropy deduced from them follow directly from the scheme of eigenvalues of the energy; the customary but unjustifiable procedure of studying the possible distributions of an assembly over the allowed levels (or the like) is not needed."

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[13] The following quotes were taken, respectively, from (1) the brief material in the preface entitled, "Note on Second Edition," (2) p. 90, and (3) p. 93 in Ref. 19.

"It is not necessary to make the much more incisive assumption which is usually made, viz. that each individual radiation oscillator always carries an integral number of quanta hv, or as is sometimes said, that there is always an integral number of photons of that particular brand in the state indicated by that individual radiation oscillator. The concept of photons or 'parcels of radiative energy'—beyond the fundamental notion of the structure of the spectrum of eigenvalues—becomes gratuitous, anyhow for the purpose of statistical mechanics."

The last two quotes are in the appendix entitled, "The Canonical Distribution of Quantum Mechanical Amplitudes," within Ref. 19. In this appendix, Schrödinger argues that the conventional scheme of counting energy states within quantum statistical mechanics can be viewed as a short-cut means for finding the canonical distribution of the amplitude squares of the eigenfunction coefficients in the Schrödinger wave function, *rather* than the probability of finding the system at some discrete energy level.

If the classical treatment of SED can be shown to be fully self-consistent, then the present work provides a deeper understanding of Schrödinger's point of view. For example, in the appendix of Ref. 19, Schrödinger starts with calculating, not the caloric entropy as discussed in the work here, but rather the probabilistic entropy $k_B \ln[\Omega(E_r)]$. The often called thermodynamic probability, Ω, is the quantity nearly universally emphasized in quantum statistical mechanics; at thermal equilibrium, Ω represents the multiplicity of the energy eigenvalue E_r, or the number of ways that energy can exist for a relatively small system when interacting weakly with a large system (a heat bath). In contrast, in the present article, changes in the caloric entropy are calculated for classical systems, based on heat flow. These changes are seen here to be equivalent to changes in the probabilistic entropy based on the eigenvalue energy scheme of Schrödinger's equation, thereby conceivably providing the deeper understanding mentioned above to Schrödinger's argument.[14]

Boyer's work in Ref. 28 first emphasized the critical need for distinguishing between these two types of entropy when consistently dealing with classical electrodynamic systems in thermal equilibrium and when developing a classical statistical mechanical description in agreement with

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[14] The following observation seems remarkable: using Schrödinger's representation of eigenfunctions provided the connection to the quantum formalism deduced here, and it is precisely Schrödinger's book on statistical mechanics[19] that expresses the closest viewpoint to the one argued here on the physical nature of thermodynamic equilibrium for "quantum mechanical systems."

nature.[15] Some of the basic postulates in traditional classical statistical mechanics appear to be flawed, not only due to the obvious disagreement between the predictions of this theory and with what we observe in nature, but also due to the internal inconsistency of the framework of traditional classical statistical mechanics as applied to systems of charged particles. For example, Refs. 8 and 28 gave a number of arguments for the requirement that fluctuating motion and fluctuating fields be present at $T = 0$ *if* thermal equilibrium can indeed exist between classical charged particles and classical electromagnetic radiation (e.g., the argument based on Earnshaw's theorem mentioned in Sec. 1). However, the framework of traditional classical thermodynamics is inconsistent with this requirement, as shown by the proof in Sec. 2.1 in Ref. 29 that the classical canonical distribution deduced in traditional classical statistical mechanics is incompatible with the existence of fluctuations at $T = 0$. The observation in Ref. 28 that caloric and probabilistic entropy are not equivalent, where the latter is calculated according to the traditional ideas of classical statistical mechanics, thus represents a *part* of this basic flaw.

Here we should note that the probabilistic entropy calculated according to the eigenvalue counting scheme of quantum statistical mechanics *does* agree with the caloric entropy calculated here following the rules of classical physics for finding changes in internal energy, work done, and heat flow, where the main assumption imposed is that of Eq. (29). Moreover, the prediction of Ref. 28 is fulfilled here in that the probabilistic entropy that results from traditional classical statistical mechanics, with its familiar canonical distribution,[28, 29] *does not* agree with the caloric entropy found here according to classical physics.

Indeed, it is fascinating to carefully go through the various quantum statistical arguments, such as in Chap. II, Chap. VI, and the appendix in Ref. 19, Chap. 11 in Ref. 30, or in the treatise of Ref. 27, and compare their subtly different quantum arguments to the significantly different classical argument here that deals with continuous energy levels. To emphasize the role of the energy eigenvalue level scheme in quantum statistical mechanics,

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[15] Boyer's work in Ref. 28 provides some early, fascinating thermodynamic arguments on the role of ZP radiation, as well as important insights to classical statistical mechanics. A few important points do need clarification and deeper analysis, however, such as in parts of Secs. III.C, G, and H, which discuss the Wien's displacement law, the Stèfan–Boltzmann law, and the relation to ZP radiation. These issues are treated in detail in Refs. 12 and 13 (in particular, see Secs. VIII and IX in Ref. 13). Also, Ref. 28 used the interesting idea of defining temperature by $\lim_{m \to \infty} \langle \frac{1}{2}mv^2 \rangle \equiv \frac{3}{2}k_B T$, which was particularly useful in the derivation of ZPP radiation in Ref. 28. However, from an axiomatic point of view, probably a more fundamental thermodynamic definition is via equating the ratio of Kelvin temperatures to the ratio of heat flow at these two temperatures, as in Eq. (3) in Ref. 12. This approach is more in line with dealing with caloric entropy, as in Ref. 12.

we note that the following procedure is typically followed:[30] "(1) Use quantum mechanics to find the ε value of the quantum states. (2) Find the partition function Z in terms of T and V. (3) Calculate the energy by differentiating $\ln(Z)$ with respect to T. (4) Calculate the pressure by ...".

In sharp contrast, rather than starting from a quantum mechanical description and then proceeding to a statistical mechanics and a thermodynamics description, here the thermal equilibrium behavior of classical electrodynamic systems was taken as the more fundamental role. A Schrödinger-like equation was introduced in Sec. 3 simply to express $P_T(\mathbf{x})$ in terms of an average over the square magnitude of an expansion in the equation's eigenfunctions. In this sense, Schrödinger's equation does not appear as some sort of fundamental (nonrelativistic, spinless, single-particle) equation of physics, but it is used more as simply a convenient representation than anything else.

Several reasons exist why thermal equilibrium behavior takes the more primary role here and Schrödinger's equation a secondary role. First, if SED is correct, then Schrödinger's equation is not "fundamental" in nature, even in the nonrelativistic, spinless, single-particle sense. Instead, Maxwell's equations and the classical equation of motion for a charged particle are the microscopic fundamental laws. As for the more "fundamental laws" governing statistical behavior, thermal equilibrium behavior must play the important role, since a near thermal equilibrium state of classical charged particles and electromagnetic fields must result if SED is correct in predicting the appearance of a quantum mechanical world around us. As an example, Refs. 8, 13, and 14 illustrated the role of thermodynamic arguments in SED by deducing the ZP spectrum at $T = 0$.

The above comments do not, by any means, imply that connections to Schrödinger's equation will not play an important role in the development of SED. After all, the behavior of nonequilibrium phenomena such as the absorption and emission of light, with all of its fascinating consequences such as line spectra and the photoelectric effect, is intimately connected with the energy eigenvalue structure of quantum mechanics.

Instead, the point being made here is that equilibrium, or near equilibrium conditions, must be of primary importance in SED and the eigenvalue structure secondary, rather than the opposite situation that occurs in quantum statistical mechanics. More specifically, consider the case when *nonequilibrium* conditions apply in quantum mechanics, such as when (using the language of quantum mechanics) an electron is raised to an excited atomic state due to energy from a directed light beam shining upon it. Provided the energy exchange is not too great to cause ionization, and depending on the particular "excited state," the atom can still remain in a relatively stable equilibrium state for a period of time that is many orders

of magnitude larger than the classical period for one orbit. This near equilibrium, or metastable state, should be the primary focus that enables at least part of the energy eigenvalue structure to be deduced.

Finally, it seems important to note the following very striking property of the Schrödinger-like equation of Eq. (23): specifically that it yields a lowest energy eigenvalue E_0 with an eigenstate $u_0(x)$ such that the probability density of $|u_0(x)|^2$ at $T = 0$ produces no heat flow during displacement operations. Setting the parameter $\mathscr{A}$ in Eq. (23) so that $|u_0(x)|^2$, the Lorentz force, or changes in E_0 agree with experimental measurements at $T \approx 0$, can be viewed as essentially setting the scale ($\hbar$) of the ZP radiation spectrum that will agree with what we observe in nature. This connection with the role of Schrödinger's equation at $T = 0$, results from the nonrelativistic expression of $\Delta \langle \mathscr{U}_{-e,\,\text{int}} \rangle$ in Eq. (20), as obtained from the classical virial theorem, and from the relation between Schrödinger's equation and the nonrelativistic quantum mechanical virial theorem via Eq. (24). Going beyond this nonrelativistic approximation for $\Delta \langle \mathscr{U}_{-e,\,\text{int}} \rangle$ may enable similar ties to be made to the relativistic treatments in quantum mechanics.

The results reported here are certainly intriguing since we see that classical physics can be pushed considerably farther than previously suspected before the ideas of SED were developed. However, one must keep in mind that only the following system was considered here, subject to some key assumptions, namely, the thermal equilibrium behavior of a classical, spinless, nonrelativistic, single charged particle in interaction with classical electromagnetic radiation and an applied electrostatic field. Hence, despite the positive results here, without a doubt considerable work remains to be done before (1) the full consistency of SED, (2) all the predictions of this theory, and (3) the correspondence of these predictions to phenomena in nature, is either established or shown to be fatally flawed.

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