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Comment on “Gauge-invariant expectation values of the energy of a molecule in an electromagnetic field” [J. Chem. Phys. 144, 044109 (2016)]

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A recent paper¹ claims that even in the absence of external fields, a certain type of time-dependent gauge transformation can result in a “molecular Hamiltonian” that is gauge-dependent. If that were so it could not correspond to a physical observable; a resolution of this difficulty is proposed. The principal calculation given in the text, and a lengthy Appendix, concerns a model where the only field is supposed to be due to the charges in the system themselves—the so-called “self-field”; this formalism is then extended to cover an applied electromagnetic (EM) field. In both cases the calculation starts from a classical Lagrangian $L$, [(9)], [(26)]² that has been known for more than a hundred years.³⁴ It contains the usual expression for the free electromagnetic field, free charged particles, and their interaction in terms of the charge-current density and the field potentials. It should be remarked at once that this Lagrangian describes a closed system⁵ so that we must have $\partial L/\partial t = 0$, and by the usual arguments, the corresponding Hamiltonian $H$ is the constant energy of the system. Why time-dependent gauge transformations in such a situation should ever be considered is not explained. It is our contention that the “problem” addressed in the paper¹ is purely an artefact of the semi-classical formalism adopted.

There is a technical difficulty for a Hamiltonian version of electrodynamics, a formulation essential for atomic and molecular physics based on the Schrödinger equation. The canonical momenta for the electromagnetic field described by (arbitrary) potentials $(\mathbf{a},\phi)$ are defined as $\mathbf{p} = \delta L/\delta \dot{\mathbf{a}}$, $\pi_0 = \delta L/\delta \dot{\phi}$. The paper¹ notes correctly that since $L$ has no terms involving $\phi$, $\pi_0 = 0$ (see [(12)]); this implies that the usual Legendre transformation from Lagrangian to Hamiltonian variables is singular.

The general solution to this problem was first formulated by Dirac⁶⁷⁻⁹⁰ it is now a textbook topic in modern quantum field theory.¹⁰¹¹ The application of the method to the electrodynamics of atoms and molecules was described in the chemical physics literature more than 40 years ago,¹²⁻¹⁴ the result given there¹³ is quite different from that proposed in the new paper,¹ and they are not at all equivalent. The scalar potential $\phi$ and its (zero) conjugate momentum $\pi_0$ are eliminated from the Hamiltonian. An obvious implication of this result is that the traditional gauge transformations in Maxwell’s theory involving the vector and scalar potentials are not possible in the Hamiltonian theory, as only the vector potential may survive. To ensure that Gauss’ law $(\epsilon_0 \nabla \cdot \mathbf{E} = \rho)$ is valid requires fixing an (arbitrary) gauge for the vector potential. Another Maxwell equation $(\nabla \cdot \mathbf{B} = 0)$ is guaranteed by the use of the vector potential, and the others follow from Hamilton’s equations of motion using modified Poisson brackets (P.B.s) appropriate to the chosen gauge. It is to be noted that the complete set of Maxwell’s equations is derived from the final Hamiltonian scheme; in Hamiltonian electrodynamics they cannot be assumed at the outset.

The paper¹ describes the transformation $L \rightarrow H$ with a method attributed to Dirac (their Ref. 84);¹⁵ comparison of their account with the above summary or better, with Dirac’s paper,¹⁵ shows that their presentation could hardly be further from Dirac’s. Some specific differences: no P.B.s are ever mentioned so time-dependence cannot be calculated without unspecified assumptions, a Lagrange multiplier is introduced to change the Lagrangian from the original $L$ [see (A1)], the scalar potential survives until the Coulomb potential appears explicitly [(A13)], and Gauss’ law is simply assumed at [(A15)]. By contrast, Dirac’s method makes no use of “Lagrange multipliers” to modify $L$, shows how P.B.s must be altered when a gauge condition is imposed so that Hamilton’s equations of motion describe the dynamics of just physical quantities, eliminates the scalar potential $\phi$ and its formal conjugate $\pi_0$, recognizes Gauss’ law as an equation of constraint, and finally does not necessarily make the Coulomb potential between pairs of particles explicit.⁸¹³ In Dirac’s original work, the final Hamiltonian is built out of only manifestly gauge-invariant quantities.¹⁵

In the non-relativistic electrodynamics of charged particles, the analogous gauge-invariant Hamiltonian that follows from Dirac’s method applied to $L$ is¹⁴

$$H = \sum_n \frac{1}{2m_n} \left| \mathbf{p}_n \right|^2 + \frac{1}{2} \epsilon_0 \int_{\mathbb{R}^3} \left( |\mathbf{E}|^2 + c^2 |\mathbf{B}|^2 \right) \, dx. \tag{1}$$

Superficially this appears to be the Hamiltonian for “free” charges and the EM field. However their interaction is carried by the P.B. relations of the momentum

$$\left[ \mathbf{p}_n, \mathbf{p}_m \right] = e_n e_{rs} B(x_n)^s, \quad \left[ \mathbf{p}_n, E(x)^s \right] = e_n e_{0} \delta_{1s} \delta^3(\mathbf{x} - \mathbf{x}_n), \tag{2}$$

where $e_{rs}$ is the usual antisymmetric Levi-Civita symbol. Since $\mathbf{p}$ behaves as $-\nabla$, (2) can be realized by setting

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\( \mathbf{p}_n = \mathbf{p}_n - e_n \mathbf{a}(x_n) \) in terms of \( \mathbf{p}_n \), the ordinary canonical momentum and \( \mathbf{a} \), the vector potential. \( \mathbf{p}_n \) is invariant to a change of gauge implemented as canonical transformation. The P.B. of \( \mathbf{E} \) and \( \mathbf{B} \) is independent of \( \mathbf{a} \). Note also that the Coulomb interaction between the charges is left implicit in the Hamiltonian (1).

It is perfectly possible to analyze the modified Lagrangian [(A1)]\(^1\) using Dirac’s generalized dynamics and we give a sketch of how this is done. The canonical momenta calculated from this \( L \) are given by [(10), (11)], and [(A3)] supplemented by an additional equation\(^16\) \( \lambda = \partial L / \partial \dot{\lambda} \equiv 0 \), since the Lagrange multiplier \( \lambda \) must be regarded as an additional independent variable. The Hamiltonian is given by [(A4)] supplemented by an extra term \( \lambda \dot{\kappa} \) with canonical P.B.s assumed

\[
\{ x_n^\mu, p_n^\mu \} = \delta_{nm} \delta_{rs}, \quad \{ a(x)^\mu, \pi(x)^\mu \} = \delta_{rs} \delta^\mu(x - x'), \quad \{ \phi(x), \pi(x)^0 \} = \delta(x - x'), \quad \{ \kappa, \lambda \} = 1. \tag{3}
\]

The Hamiltonian is then transformed to the weak equation

\[
H = \frac{1}{2} \sum_n m_n \dot{x}_n^2 + \frac{1}{2} e_0^2 \int_{\mathbb{R}^3} \left( \pi^2 + e_0^2 c^2 |\mathbf{B}|^2 \right) dx + \int_{\mathbb{R}^3} \phi (\rho + \nabla \cdot \pi) dx + e^2 \sum_{i=1}^3 \pi_0(i \nabla \cdot \mathbf{a} - f) dx + \frac{\epsilon}{\kappa} \int_{\mathbb{R}^3} \pi_0^2 dx + \kappa \lambda. \tag{4}
\]

Here \( \dot{x}_n = \frac{1}{m_n} (\mathbf{p}_n - e_n a(x_n)) \) is the gauge-invariant “velocity” (see (2)), an integration by parts is used to obtain the third term, and we retain \( \pi_0 \) since its identification with \( -e_0 \mathbf{E} \) can only be established after the constraints have been dealt with. \( \rho \) is the charge density.

We do this as follows: the Hamiltonian describes the system at an instant in time and one must first check using the Hamiltonian equation of motion, \( \dot{X} = \{ X, H \} \) that the constraint \( \Omega_1 \equiv \lambda \approx 0 \) is valid for all time, i.e., we require \( \lambda \equiv 0 \). We have

\[
0 = \lambda = \{ \lambda, H \} = -\frac{e^2}{\kappa^2} \int_{\mathbb{R}^3} \pi_0^2 dx \Rightarrow \pi_0 \approx 0 \tag{5}
\]

since for any weak equality\(^8\) \( A \approx 0, A^2 \approx 0 \). The last relationship in (5) is a further constraint we denote as \( \Omega_2 \); for consistency the time derivative of \( \Omega_2 \) must vanish, at least weakly,

\[
0 = \dot{\pi}_0 = \{ \pi_0, H \} = \rho + \nabla \cdot \pi \approx 0. \tag{6}
\]

The RHS is another constraint, and we denote it as \( \Omega_3 \). Again the time derivative of \( \Omega_3 \) must vanish; we compute

\[
0 = \Omega_3 = \{ \rho + \nabla \cdot \pi, H \} = -c^2 \pi_0 (\nabla \cdot \pi, \nabla \cdot \mathbf{a}) = c^2 \pi_0 \nabla^2 \delta^\lambda(x - x') = 0. \tag{7}
\]

because of (5), and so, we have all the constraints accounted for consistently.

The constraints here have the important property that their mutual P.B. relations and those with \( H \) are all zero. According to Dirac’s method, they may be incorporated in the Hamiltonian with completely arbitrary coefficients without affecting the physics;\(^2\) it follows that the last three terms in Equation (4) can all be set to zero, and \( \phi \) can be replaced by an arbitrary coefficient, say \( u(x) \) (its conjugate has been properly eliminated, and so, \( \phi \) has no dynamics). There are various ways to deal with this modified term which have been described in detail previously.\(^{14}\) One can pass directly to (1) where now the electric field is properly identified or one can either introduce a gauge condition on the vector potential or impose Gauss’s law as a constraint on the quantum states.

It suffices to say that only in the Coulomb gauge does \( \mathbf{E} \) decompose into simply the static Coulomb interaction between charges (required for the molecular Hamiltonian) and the transverse electric field associated with radiation. In any other gauge there is an extra singular contact interaction energy.\(^{5,14,15,17,18}\) The “semi-classical” radiation model (quantized atom + classical EM field described by Maxwell’s equations) is a popular and useful ansatz for practical calculations; in order to set it up, one must first select the Coulomb gauge to eliminate the contact interaction since there is simply no way to deal with it in such a model. However if (1) is treated as a microscopic classical model, the expected classical equations of motion are obtained so that there is no difficulty. Equally, if (1) is fully quantized (particles and EM field), its S-matrix, which contains all experimentally observable cross sections, is independent of this singular term.\(^{14}\)

\( ^{15} \)An equation (N) in Ref. 1 is denoted here by [\( (N) \)]; we prefer to use \( x_n^\mu \) for the \( r \)th component of the coordinate for particle \( n \) and generally suppress the space-time variables in the field quantities to simplify notation.
\( ^{17} \)W. Heitler, The Quantum Theory of Radiation (Clarendon Press, Oxford, 1936), and numerous later printings/editions.
\( ^{29} \)This is a special use of the symbol \( \approx \) to denote “weak equality” in the sense of constrained Hamiltonian dynamics;\(^{8,11}\) it has nothing to do with “approximation.”