Gauge-invariant expectation values of the energy of a molecule in an electromagnetic field

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For a molecule interacting with an electromagnetic field, we show that the Hamiltonian can be separated into a molecular Hamiltonian and a field Hamiltonian, both with *gauge-invariant* expectation values.[1] The expectation value of the molecular Hamiltonian gives physically meaningful result for the energy of a molecule in a time-dependent field. The usual partitioning of the full Hamiltonian results in gauge dependence of both the molecular Hamiltonian and the field Hamiltonian.[2,3] With the usual partitioning of the Hamiltonian, gauge dependence arises even in the absence of an applied field, as we have shown explicitly by considering a gauge transformation from zero applied field and zero external potentials to zero applied field, but non-zero vector and scalar potentials.[1,4] By repartitioning the full Hamiltonian, we resolve this problem and also remove the gauge-dependence from the Hamiltonian for a molecule in a non-zero applied field.[1] We treat the electromagnetic field classically and treat the molecule quantum mechanically, but nonrelativistically. We construct the full Hamiltonian using a Lagrange multiplier method originally suggested by Fermi[5] and later applied by Goldman,[6] partition this Hamiltonian into a molecular term H_m and a field term H_f, and then show that both H_m and H_f have gauge-invariant expectation values.[1] Any gauge may be chosen for the calculation; but following our partitioning, the expectation values of the molecular Hamiltonian are identical to those obtained in the Coulomb gauge. As a corollary of this result, the power absorbed by a molecule from a time-dependent, applied electromagnetic field is equal to the time-derivative of the nonadiabatic term in the molecular energy, in any gauge.[7,8]

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