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S. T. Epstein

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by

S. T. Epstein *

Theoretical Chemistry Institute

University of Wisconsin

Madison, Wisconsin 53706

ABSTRACT

The well known relationship between gauge invariance and current conservation is exhibited within the usual quantum mechanical formalism. It is then shown that the use of Gauge Invariant Atomic Orbitals does not necessarily lead to the expected current conservation. The reason is found to lie in the constrained nature of the gauge invariance which is provided by the use of GIAO's. It is concluded that this invariance is, of itself, no argument in favor of their use.

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I. INTRODUCTION

If one views the Schroedinger equation from the point of view of Lagrangian field theory, then there is a well known[1] connection between gauge invariance and current conservation. In the next section of this paper we will establish a similar connection within the ordinary quantum mechanical formalism. In the third section we then show that the use of gauge invariant atomic orbitals (GIAO's)[2] does not necessarily lead to the expected current conservation, and the reason is discussed. This then leads us in the fourth section to examine in detail the nature of the gauge invariance which is provided by the use of GIAO's. We conclude that, contrary to what is probably the generally accepted view, this invariance is, of itself, no argument in favor of their use. The body of the paper is concerned with static fields and with energy eigenfunctions. An appendix is then devoted to a discussion of time dependent situations.

II. GAUGE INVARIANCE AND CURRENT CONSERVATION

We consider the problem of N non-relativistic electrons moving in external static electric and magnetic fields, and we confine attention to energy eigenstates. We now make use of the following general criterion of invariance: Since the formalism of quantum mechanics is invariant to unitary transformations of wave functions, one will have invariance to particular transformations if these can be shown to lead to unitary transformations. It is well known that gauge transformations meet this criterion. Namely if the vector potential undergoes a gauge transformation

$$\vec{A}(\vec{r}) \rightarrow \vec{A}'(\vec{r}) = \vec{A}(\vec{r}) + \vec{\nabla} \lambda(\vec{r})$$

where λ is some real function, then the wave function undergoes the unitary transformation

$$\psi(\vec{A}') = e^{-i\Lambda} \psi(\vec{A}) \tag{1}$$

and correspondingly the Hamiltonian also undergoes a unitary transformation

$$H(\vec{A}') = e^{-i\Lambda} H(\vec{A}) e^{i\Lambda} \tag{2}$$

where (we use atomic units and c is the velocity of light)

$$\Lambda = \frac{1}{c} \sum_{i=1}^{N} \lambda(\vec{r}_i) \tag{3}$$

In particular we will be concerned with families of gauge transformations

$$\lambda(\vec{r}) = \sum_{\alpha} \epsilon_\alpha \lambda_\alpha(\vec{r}) \tag{4}$$

where the ϵ_α are arbitrary real numbers, and where the λ_α are some given real functions.

If now we expand $H(\vec{A}')$ in powers of the ϵ_α we find through first order in the ϵ_α

$$H(\vec{A}') = H(\vec{A}) - i [\Lambda, H(\vec{A})] + \cdots \tag{5}$$

where [,] denotes the commutator. Then from first order perturbation theory, the first order change in the energy is given by $\sum_\alpha \epsilon_\alpha E_\alpha^{(1)}$ where

$$E_\alpha^{(1)} = -i\left(\psi(\vec{A}),\ [\Lambda_\alpha, H(\vec{A})]\psi(\vec{A})\right) \tag{6}$$

and where

$$\Lambda_\alpha = \frac{1}{c}\sum_{i=1}^{N} \lambda_\alpha(\vec{r}_i)$$

However since (2) is a unitary transformation of H, the energy is gauge invariant, whence $E_\alpha^{(1)}$ must vanish. Therefore we must have

$$\left(\psi(\vec{A}),\ [\Lambda_\alpha, H(\vec{A})]\psi(\vec{A})\right) = 0 \tag{7}$$

which is of course true since $H(\vec{A})\psi(\vec{A}) = E\psi(\vec{A})$. Thus the hypervirial theorem[3] (7) can be viewed as being a consequence of gauge invariance.

It is now easy to show, after some integrations by parts, that (7) can be written as

$$\int d\vec{r}\ \vec{\nabla}\cdot\vec{j}\,\lambda_\alpha = 0 \tag{8}$$

where $\vec{j}$ is the one-electron current. Then since (8) is to hold for all λ_α we have

$$\vec{\nabla}\cdot\vec{j} = 0 \tag{9}$$

i.e., current conservation.[4]

So far all our discussion has concerned exact wave functions. We now quote two relevant results for variational wave functions:

(i) If the set of trial functions is invariant to the set of gauge transformations $e^{-i\Lambda}$ then[5] the optimal trial functions will satisfy the hypervirial theorems (7) and hence (8).

(ii) We will have gauge invariance in the sense that if we use this same set of trial functions with both $H(\vec{A})$ and $H(\vec{A}')$ then[6] we will get the same energies, and also the optimal trial functions will be related by formulae like (1).

In particular it is easy to show[7] that unrestricted coupled Hartree-Fock theory meets these conditions for all λ_α, and indeed in this theory the energies are gauge invariant, and the one electron current is conserved.[8] However in most variational calculations this will not be the case.[9]

III. GIAO'S AND CURRENT CONSERVATION

For clarity we will consider a very simple system: a single electron moving in the field of two fixed centers, and in a uniform magnetic field $\vec{B}$. Further, in accord with what seems to be the custom in quantum chemistry, we will confine attention to a very special class of gauge transformations. Namely for the vector potential we take

$$\vec{A} = \tfrac{1}{2}\,\vec{B}\times\vec{r} \tag{10}$$

and then confine attention to the gauge transformations

$$\vec{A} \to \vec{A}' = \tfrac{1}{2}\,\vec{B}\times\vec{r} + \vec{\nabla}\,\tfrac{1}{2}\,\vec{B}\times\vec{d}\cdot\vec{r} \tag{11}$$

where $\vec{d}$ is an arbitrary constant vector. From (11) we have

$$\vec{A}' = \tfrac{1}{2}\,\vec{B}\times(\vec{r}+\vec{d}) \tag{12}$$

whence we are considering only changes of gauge origin. Further we have

$$\lambda = \frac{1}{2}(\vec{B}\times\vec{d})\cdot\vec{r} \tag{13}$$

so that we can evidently identify the ϵ_α of Section II with the components of $\vec{d}$. Since we are considering only a restricted class of gauge transformations we will not be concerned with full current conservation (9), but only with (7) for λ_α given by (13). Evaluating the commutator one finds that (7) then is the statement that the average electron velocity, the electron velocity operator being

$$\vec{\pi} \equiv \vec{p} + \frac{1}{c}\vec{A} \tag{14}$$

must vanish in directions perpendicular to $\vec{B}$.

Turning now to GIAO's, for our problem the simplest approximate wave function which is in accord with the GIAO ideas[2] would be

$$\psi^A = e^{-\frac{i}{c}\vec{A}(\vec{R}_1)\cdot\vec{r}}\phi_1 + \alpha e^{-\frac{i}{c}\vec{A}(\vec{R}_2)\cdot\vec{r}}\phi_2 \tag{15}$$

where $\vec{R}_1$ and $\vec{R}_2$ are the positions of the centers, ϕ_1 and ϕ_2 are field independent s-functions centered on $\vec{R}_1$ and $\vec{R}_2$ respectively, and α is some number.[10] To simplify calculations we will choose our Cartesian coordinate system[11] so that $\vec{R}_1 = (0,0,0)$ and $\vec{R}_2 = (0,0,R)$. Also we will choose $\vec{B}$ to be in the x-direction. Thus we have and

$$\vec{A} = \left(0, -\frac{Bz}{2}, \frac{By}{2}\right)$$

$$\psi^A = \phi_1 + \alpha e^{i\frac{RB}{2c}y}\phi_2$$

Now since the use of GIAO's is known to give gauge invariant energies (we discuss this further in the next section) one might suppose, from our earlier discussions, that one would necessarily have

$$(\psi^A, \pi_y \psi^A) = 0 \tag{17}$$

and

$$(\psi^A, \pi_z \psi^A) = 0 \tag{18}$$

We will now show that this is not the case.

First we consider (18). One readily finds that

$$(\psi^A, \pi_z \psi^A) = (\phi_1, (p_z + \frac{yB}{2c})\phi_1) + |\alpha|^2 (\phi_2, (p_z + \frac{yB}{2c})\phi_2) +$$

$$+ [\alpha (\phi_1, e^{i\frac{BR}{2c}y}(p_z + \frac{yB}{2c})\phi_2) + c.c.] \tag{19}$$

Our assumption that ϕ_1 and ϕ_2 are s-states then makes the first line of (19) vanish, and allows the second line to be written as

$$i(\alpha - \alpha^*)\left[-(\phi_1, (\cos\tfrac{BR}{2c}y)\tfrac{\partial\phi_2}{\partial z}) + (\phi_1, \tfrac{yB}{2c}(\sin\tfrac{BR}{2c}y)\phi_2)\right]$$

We now note that for $\vec{B} = 0$ the expression in the brackets becomes

$$-(\phi_1, \frac{\partial\phi_2}{\partial z})$$

which in general doesn't vanish. Therefore (19) will in general vanish only if α is real.

We now turn attention to $(\psi^A, \Pi_y \psi^A)$. Then assuming α real and invoking the symmetry of ϕ_1 and ϕ_2 one readily finds that

$$(\psi^A, \Pi_y \psi^A) = 2\alpha \left[\left(\phi_1, \left(\sin \frac{BR}{2c} y\right) \frac{\partial \phi_2}{\partial y}\right) + \left(\phi_1, \frac{B}{2c}(R-z)\left(\cos \frac{BR}{2c} y\right)\phi_2\right)\right]$$

and in order for this to vanish the bracket must vanish (unless $\alpha = 0$) which seems unlikely. In particular if we expand in powers of B the leading term in the bracket is

$$\frac{BR}{2c}\left[\left(\phi_1, y \frac{\partial \phi_2}{\partial y}\right) + \left(\phi_1, \left(1 - \frac{z}{R}\right)\phi_2\right)\right] \tag{20}$$

and there seems no reason for even this to vanish, and indeed a calculation with Gaussians

$$\phi_1 = \text{const}\, e^{-\beta(x^2 + y^2 + z^2)}$$

$$\phi_2 = \text{const}\, e^{-\gamma(x^2 + y^2 + (R-z)^2)}$$

yields a non vanishing result (unless $\beta = \gamma$) . Therefore we conclude that in this particular example we cannot have both (17) and (18), and hence we conclude that in general the use of GIAO's does not guarantee such theorems.

The reason for this failure is not hard to find. As stated in (i) of Section II, the theorems will hold if the set of trial functions is invariant to the appropriate gauge transformation. However our set, which (for fixed α , ϕ_1 and ϕ_2 [10]) consists of the single function ψ^A , evidently changes under the gauge transformation (12): Namely from (15) we have

$$\psi^{A'} = e^{-\frac{i}{c}\vec{r}\cdot\vec{\lambda}}\psi^{A} = e^{-\frac{i}{c}\lambda}\psi^{A} \qquad (21)$$

Thus the conditions of (i) are not met and so the theorems don't hold.[12]

Another, equivalent, reason for failure, one which makes direct contact with (6) (the argument above of course dealt directly with (7)), is the following: First order perturbation theory in the form of equation (6), is a special case of the generalized Hellmann-Feynman theorem for the parameter ϵ_α. Now one knows[13] that this theorem will also hold in variational calculations provided that the set of trial functions is independent of the ϵ_α. Evidently this is not the case here. Thus the first order energy change is not given by a formula like (6) but rather by one which contains extra terms, and therefore although the first order energy change does vanish in accord with gauge invariance, that vanishing does not lead to (7).

These considerations naturally raise the question: what then is the nature of the gauge invariance which is provided by the use of GIAO's? It is this question that we now turn.

IV. GIAO'S AND GAUGE INVARIANCE

Clearly the fact that ψ^{A} changes with $\vec{A}$, the fact which led to the failure in the previous section, is precisely the feature of ψ^{A} which leads to the gauge invariance of the energy. Thus the transformation (21) is exactly the transformation (1) (for a one electron problem) and hence one has

$$\frac{(\psi^{A'}, H(A')\psi^{A'})}{(\psi^{A'}, \psi^{A'})} \simeq \frac{(\psi^{A}, H(A)\psi^{A})}{(\psi^{A}, \psi^{A})}$$

i.e., the energy is gauge invariant. However having recognized that the gauge invariance is guaranteed by the way in which the orbitals change with gauge,[14] we then note that by a similar device we can make any calculation equally gauge invariant. Thus for example consider instead of ψ^A the function

$$\bar{\psi}^A = e^{-\frac{i}{c}\vec{A}(\vec{\rho}_1)\cdot r}\phi_1 + \alpha e^{-\frac{i}{c}\vec{A}(\vec{\rho}_2)\cdot r}\phi_2$$

where $\vec{\rho}_1$ and $\vec{\rho}_2$ are any given vectors. Then since we have

$$\bar{\psi}^{A'} = e^{-\frac{i}{c}\lambda}\bar{\psi}^A$$

a calculation based on $\bar{\psi}$ will also yield a gauge invariant energy. In particular if we choose $\vec{\rho}_1 = \vec{\rho}_2 = 0$ then evidently we could conclude that even the use of simply

$$\phi_1 + \alpha\phi_2$$

with $\vec{A} = \frac{1}{2}\vec{B}\times\vec{r}$ and $e^{-\frac{i}{c}\vec{A}(0)\cdot\vec{r}}(\phi_1 + \alpha\phi_2)$ otherwise, will yield gauge invariant results.

More generally it is clearly always possible to get such, what we might call "enforced gauge invariance" or "constrained gauge invariance", for the energy calculated using any set of trial functions whatsoever in any one gauge simply by changing the trial function appropriately as one changes gauges (or equivalently, by always returning to the original gauge to do the calculation). Further it would seem that if one proceeds in this way, and as we have seen in using GIAO's one does precisely this,[15]

that then the resulting gauge invariance should not be thought to lend any special credance to the calculation since requiring it has simply led to a specified connection between the sets of trial functions to be used in different gauges. Rather one's a priori expectations concerning the accuracy of the calculation, i.e., one's a priori expectations concerning the physical completeness of the set in any one gauge, must clearly be based on other considerations. In contrast, if in the spirit of (i) and (ii) of Section II, the set of trial functions is invariant to gauge transformations, then equally clearly this is a relevant piece of information since evidently it does supply some information concerning the completeness of the set.

Now in fact, as is well known, there is a real physical basis for the use of GIAO's: The function $e^{-\frac{i}{2}\vec{A}(\vec{R})\cdot\vec{r}}\phi_i$ is, through first order in $\vec{B}$, the exact eigenfunction of a one-electron one-center plus uniform magnetic field problem which for $\vec{B} = 0$ has ϕ_i as an eigenfunction.[16] Moreover we would emphasize that nothing we have said about "constrained" or "enforced" gauge invariance should obscure this point. Rather we are saying that this, and not the resulting gauge invariance, is what suggests that the use of GIAO's may be an effective tool in dealing with problems of molecules in uniform magnetic fields. On the other hand, of course, the failures which we have discussed are also real and should be weighed in the judgement.

Returning to our special example, since any choice of $\vec{\rho}_1$ and $\vec{\rho}_2$ will yield a gauge invariant energy, which however depends on $\vec{\rho}_1$ and $\vec{\rho}_2$, it is natural to ask for the best $\vec{\rho}_1$ and $\vec{\rho}_2$ in the

sense of the variation principle. To find out we of course simply let $\vec{\rho}_1$ and $\vec{\rho}_2$ be variational parameters. It is then of interest to note that the resultant set of trial functions is now invariant to gauge transformations since $\Psi^{A'}$ can be gotten from Ψ^{A} by replacing $\vec{\rho}_1$ and $\vec{\rho}_2$ by $\vec{\rho}_1+\vec{a}$ and $\vec{\rho}_2+\vec{a}$ respectively, so that a gauge transformation simply turns one trial function into another. Thus from (i) and (ii) of Section II it follows that by introducing this extra freedom[17] we will ensure that (17) and (18) are now satisfied (evidently therefore in our example the optimal $\vec{\rho}_1$ and $\vec{\rho}_2$ are <u>not</u> (0,0,0) and (0,0,R)), and also we will still have gauge invariant energies and properly gauge variant wave functions, but now in an unforced way (one uses the <u>same</u> set of trial functions in <u>all</u> gauges) rather than by constraint.

V. ACKNOWLEDGEMENTS

I am indebted to audiences in England (Nottingham, Oxford, and Sheffield) and in my own univeristy for having suffered through, and for having commented on, various versions of this material.

APPENDIX

Although in the body of the paper we are concerned only with stationary states it would seem useful to add some comments on the time dependent case. Here under a gauge transformation the vector and scalar potentials change according to

$$\vec{A} \rightarrow \vec{A}' = \vec{A} + \vec{\nabla}\lambda$$

$$\Phi \rightarrow \Phi' = \Phi - \frac{1}{c}\frac{\partial \lambda}{\partial t} \qquad \text{(A-1)}$$

Again invariance is expressed by the fact that the wave function undergoes a unitary transformation

$$\psi(\vec{A}', \Phi') = e^{-i\Lambda}\psi(\vec{A}, \Phi) \qquad \text{(A-2)}$$

and correspondingly

$$H(\vec{A}', \Phi') = e^{-i\Lambda} H(\vec{A}, \Phi) e^{i\Lambda} + \frac{1}{c}\frac{\partial \Lambda}{\partial t} \qquad \text{(A-3)}$$

where

$$\Lambda = \sum_{i=1}^{N} \lambda(\vec{r}_i, t)$$

If now we choose

$$\lambda(\vec{r}, t) = \sum_{\alpha} \epsilon_\alpha \lambda_\alpha(\vec{r}, t)$$

then the analogue of the result (6) for the first order energy change is provided by the time dependent Hellmann-Feynman theorem[18] which yields a relation between the change in ψ and the change in H, due to a change in a parameter, whatever the nature of that change may be. As we have emphasized, gauge invariance is expressed by the particular nature of the changes (A-2) and (A-3), in particular by the fact that (A-2) is a unitary transformation. For our particular case then the general theorem

$$i\frac{d}{dt}\left(\psi, \frac{\partial \psi}{\partial \sigma}\right) = \left(\psi, \frac{\partial H}{\partial \sigma}\psi\right)$$

where σ is a real parameter yields

$$\frac{d}{dt}(\Psi, \Lambda_\alpha \Psi) = (\Psi, \frac{\partial \Lambda_\alpha}{\partial t}\Psi) + i(\Psi, [H, \Lambda_\alpha]\Psi) \qquad \text{(A-4)}$$

This result, a special case of the generalized Ehrenfest's theorem or time dependent hypervirial theorem, is of course a well known consequence of the Schröedinger equation. However we now see that it can also be regarded as a consequence of gauge invariance, and evidently in the time independent case, and with the $\epsilon_\alpha = 0$, it reduces to (7). Further it is easy to show that (A-4) can be rewritten as

$$\int d\vec{r} \left(\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \vec{j} \right) \lambda_\alpha = 0 \qquad \text{(A-5)}$$

where ρ is the one electron density. Then since (A-5) is true for all λ_α we have

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \vec{j} = 0$$

i.e., current conservation.

All this is for exact wave functions. For variational wave functions one can show[19] in complete analogy to the static case, that if the set of trial functions is invariant to the set of gauge transformations then the optimal trial functions will satisfy (A-4). This condition is met by unrestricted coupled Hartree-Fock theory for all λ_α and hence one has current conservation in that theory.

FOOTNOTES AND REFERENCES

1. See for example W. Pauli, Rev. Mod. Phys. 13, 203 (1941).
2. GIAO's were first introduced by F. London, J. Phys. Rad. 8, 307 (1937). The recent paper by R. Ditchfield, J. Chem. Phys. 56, 5688 (1972) contains an extensive bibliography.
3. J. O. Hirschfelder, J. Chem. Phys. 33, 1762 (1960).
4. One can of course consider more general unitary transformations. For example, at the other extreme, with Λ an arbitrary function of all coordinates, one is led to
$$\int d\vec{r}_1 \cdots d\vec{r}_N \left[\vec{\nabla}_1 + \vec{\nabla}_2 + \cdots\right] \cdot \vec{J}\, \Lambda = 0$$
and hence
$$\left[\vec{\nabla}_1 + \vec{\nabla}_2 + \cdots\right] \cdot \vec{J} = 0$$
where $\vec{J}$ is the N-electron current.
5. S. T. Epstein and J. O. Hirschfelder, Phys. Rev. 123, 1495 (1961).
6. S. T. Epstein, J. Chem. Phys. 42, 2897 (1965).
7. One uses the same set of trial functions - the set of all Slater determinants - in any gauge, and this set is invariant to all gauge transformations. (See Ref. 6).
8. Our statement of course refers to total current. The individual orbital currents are not in general conserved.
9. The work reported in this section stems in part from a conversation with Professor R. McWeeny in which he raised the question of current conservation in variational calculations.
10. Strictly speaking these symmetry restrictions on ϕ_1 and ϕ_2 are irrelevant for the questions we are considering. Also irrelevant is the question whether or not α, ϕ_1 and ϕ_2 are determined variationally, so we will treat them as given.

11. R. McWeeny, Chem. Phys. Lett. 9, 341 (1971) has discussed some aspects of the question of invariance to choice of coordinates (rotating or translating the coordinate system of course also involves unitary transformations). We will not enter into a discussion of such matters here except to note that similar considerations applying as in the case of gauge invariance

12. As derived in Ref. 5 these conditions are only sufficient conditions. However in practice they, and others like them, seem usually to be necessary unless symmetry and reality considerations intervene.

13. A. C. Hurley, Proc. Roy. Soc. A226, 179 (1954).

14. They might therefore be better called gauge variant atomic orbitals.

15. Unless the set of atomic orbitals is essentially complete, but in such a case the use of the gauge factors become irrelevant anyway.

16. That is with the gauge origin at the center, the eigenfunctions of the one electron problem are unchanged through first order in B (more precisely they are the zero field eigenfunctions whose orbital angular momenta are quantized along $\vec{B}$).

17. For the purpose of invariance of the set, it would already suffice to use $e^{-\frac{i}{c}A(\vec{\beta})\cdot\vec{r}}[\phi_1 + a\phi_2]$ with $\vec{\beta}$ as a variational parameter.

18. E. F. Hayes and R. G. Parr, J. Chem. Phys. 43, 1831 (1961).

19. S. T. Epstein, J. Chem. Phys. 45, 385 (1966); S. T. Epstein and R. E. Johnson, J. Chem. Phys. 51, 188 (1969).