INTERNATIONAL JOURNAL OF QUANTUM CHEMISTRY, VOL. XII, 227–229 (1977)

A Note on Differences Between Operator-Level and Function-Level Equations of Motion

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The primary purpose of this note is to demonstrate that there are important differences between the operator and function equalities which arise in using the Heisenberg equation of motion [1] (EOM) in many-body physics and chemistry. The pedagogical remarks presented here are offered in the hope that they will help others to avoid drawing false conclusions because of a lack of understanding.

Let us begin by assuming that we are treating a system which consists of electrons moving in the potential field $V(\vec{r})$ of one or more fixed positively charged nuclei, such as would be the case for electrons in a molecule. Then the many-electron Hamiltonian H can be written in second quantization notation [2] (in atomic units) as

$$H = \sum_{i,j} \langle \phi_i | -\tfrac{1}{2}\nabla_r^2 + V(\vec{r}) | \phi_j \rangle a_i^\dagger a_j + \tfrac{1}{2} \sum_{ijkl} \langle \phi_i \phi_j | r_{12}^{-1} | \phi_k \phi_l \rangle a_i^\dagger a_j^\dagger a_l a_k \tag{1}$$

where the basis spin orbitals $\{\phi_i\}$ are assumed to be complete and orthonormal and the $a_i^\dagger$ and a_j are Fermion creation and annihilation operators [2], respectively. Nowhere in H does there appear a reference to the number of electrons. In fact, the above H is an operator within the spaces of any number of electrons (for fixed nuclear potential $V(\vec{r})$). For example, the same second-quantized Hamiltonian is involved in the electronic problems of F^-, F, F^+, F^{+2}, etc. Such a Hamiltonian can be expressed formally in terms of its exact orthonormal eigenstates $\{\psi_K^{(N)}\}$ as $H = \sum_{N=0}^{\infty} \sum_K E_K^{(N)} |\psi_K^{(N)}\rangle \langle \psi_K^{(N)}|$. Because H commutes with the "total number of electrons" operator $\hat{N} = \sum_i a_i^\dagger a_i$, its eigenstates can be labeled by their electron number N as in $\psi_K^{(N)}$. The subscript K will be used to label the energy $E_K^{(N)}$ and all other good quantum numbers of $\psi_K^{(N)}$. We assume that this K index is sufficiently complete to uniquely label each state, even within degenerate-energy manifolds.

Now suppose that we were able to find an excitation operator $O_L^\dagger(N, M)$, which operates on the lowest energy* M-electron state $\psi_0^{(M)}$ to give the Lth N-electron state, $O_L^\dagger(N, M)$ will obey the function equation

$$[H, O_L^\dagger(N, M)]\psi_0^{(M)} = \Delta E_L(N, M) O_L^\dagger(N, M) \psi_0^{(M)} \tag{2}$$

where $\Delta E_L(N, M)$ is an eigenenergy of this equation. This equation is the common starting point [1] of EOM methods whose goal is the calculation of electronic [3] or nuclear excitation energies as well as electronic ionization [4] energies. Let us enquire as to how $O_L(N, M)$ could be expressed (formally) in terms of the complete set† of ket-bra operators $\{|\psi_J^{(P)}\rangle \langle \psi_I^{(Q)}|; P, Q = 0, 1, \ldots \infty; I, J = 0, 1, 2, \ldots\}$. By expanding $O_L^\dagger(N, M)$ as $\sum_{I,J=0}^{\infty} \sum_{P,Q=0}^{\infty} (P, Q; J, I | L; M, N) |\psi_J^{(P)}\rangle \langle \psi_I^{(Q)}|$, inserting this into Eq. (2), and equating coefficients of the linearly independent ket-bra operators, we obtain

$$O = (P, M; J, O | L, M, N)(E_J^{(P)} - E_0^{(M)} - \Delta E_L(N, M)) \tag{3}$$

* We only choose this state as a specific example because it is the most common choice in many-body theory; our arguments will hold for other states as well.

† Since the set of eigenfunctions $\{\psi_K^{(N)}\}$ of H is complete, any operator A can be rewritten as $\sum_{N,M=0}^{\infty} \sum_{K,L=0}^{\infty} |\psi_K^{(N)}\rangle \langle \psi_K^{(N)}| A |\psi_L^{(M)}\rangle \langle \psi_L^{(M)}|$ by making use of the completeness relation twice. Thus, just as the set $\{\psi_K^{(N)}\}$ was sufficient to expand any function, $\{|\psi^{(N)}\rangle \langle \psi_L^{(M)}|\}$ is sufficient to expand any operator A.

for all P and all J. Thus all of the expansion coefficients $(P, M; J, O|L, M, N)$ must vanish, except for $P = N$ and $J = L$, in which case the desired eigenenergy difference is $\Delta E_L(N, M) = E_L^{(N)} - E_0^{(M)}$. We conclude that $O_L^\dagger(N, M)$ can then be expressed as

$$(N, M; L, O|L, M, N)|\psi_L^{(N)}\rangle\langle\psi_0^{(M)}| + \sum_{\substack{O,I\neq M,O \\ Q,P,I,J}} (P, Q; J, I|L, M, N)|\psi_J^{(P)}\rangle\langle\psi_I^{(Q)}|$$

and the assumption that $O_L^\dagger(N, M)\psi_0^{(M)} = \psi_L^{(N)}$ tells us that $(N, M; L, O|L, M, N) = 1$. The other expansion coefficients $(P, Q; I, J|L, M, N)$ for $Q, I \neq M, O$ can *not* be determined either by $O_L^\dagger(N, M)\psi_0^{(M)} = \psi_L^{(N)}$ or by the EOM [Eq. (2)]; they remain unknown. Thus because of these unknown components of $O_L^\dagger(N, M)$, there is a lack of uniqueness (or perhaps a presence of useful flexibility) in the solutions to Eq. (2). Even the (extra) condition that the adjoint of $O_L^\dagger(N, M)$ should annihilate $\psi_0^{(M)}(O_L(N, M)\psi_0^{(M)} = 0)$, which is often introduced as an additional constraint or as a mechanism for determining that reference state $\psi_0^{(M)}$ which is consistent [1] with a *given* $O_L^\dagger(N, M)$, does not allow $O_L^\dagger(N, M)$ to be uniquely specified. It only forces the coefficients $(M, Q; O, I|L, M, N)(Q, I \neq M, O)$ to vanish. The $(P, Q; J, I|L, M, N)$ $(P, J \neq M, O; Q, I \neq M, O)$ are still undetermined.

If, instead of attempting to solve Eq. (2), which is an equation involving functions, we seek solutions $O_L^\dagger$ to the *operator* equation of motion [5, 6]

$$[H, O_L^\dagger] = \Delta E_L O_L^\dagger \tag{4}$$

then the expansion of $O_L^\dagger$ as $\sum_{P,Q;J,I}(P, Q; J, I|L)|\psi_J^{(P)}\rangle\langle\psi_I^{(Q)}|$ when substituted into Eq. (4) yields

$$(P, Q; J, I|L)(E_J^{(P)} - E_I^{(Q)} - \Delta E_L) = 0 \tag{5}$$

for all P, Q and all J, I. Then all but one of the expansion coefficients $(P, Q; J, I|L)$ must vanish; the one for which $\Delta E_L = E_J^{(P)} - E_I^{(Q)}$ need not vanish. In the case of energy level degeneracies, which will not be further considered here, more than one of the coefficients can be nonzero. Therefore, in the case of the operator EOM, we can conclude that the excitation operator $O_L^\dagger$ can be written in terms of a *single* ket-bra $O_L^\dagger = (P, Q; J, J|L)|\psi_J^{(P)}\rangle\langle\psi_I^{(Q)}|$ and $E_L = E_J^{(P)} - E_I^{(Q)}$. The coefficient $(P, Q; J, I|L)$ is arbitrary $(\neq 0)$. Clearly, Eq. (4) is a much stronger statement than that contained in Eq. (2). Equation (4) is required to be valid in the operator sense, i.e., as it operates on *any* of the complete set of eigenstates $\{\psi_S^{(R)}\}$ of H. Equation (2) requires that the operators $[H, O_L^\dagger(N, M)]$ and $\Delta E_L(N, M)O_L^\dagger(N, M)$ give equal results when operating on the *single* function $\psi_0^{(M)}$. Therefore, it is not surprising that the much more stringent requirements imposed by Eq. (4) greatly decreases the nonuniqueness (or flexibility) which occurs in the resultant excitation operators. Because, in stating the operator EOM [Eq. (4)], we do not introduce a reference function to fill the role that $\psi_0^{(M)}$ played in Eq. (2), we do not have any analog of the extra constraint $O_L(N, M)\psi_0^{(M)} = 0$ which was discussed above.

The above conclusions regarding the uniqueness of the solutions to Eq. (4) and the lack of uniqueness of solutions to Eq. (2) are drawn only for the exact excitation operators. For almost all many-body Hamiltonians of interest, neither Eq. (2) nor Eq. (4) can be solved exactly. In actual calculations one most likely would attempt to find a solution to one of the above equations which is valid through some (chosen) order in perturbation theory [5]. However, the fact that there is, as demonstrated above, a great deal of difference between the nature of the respective solutions of Eqs. (2) and (4) implies that there will also be major differences between perturbative solutions to these equations (if the perturbation series converge). Therefore, when formulating physical problems within an EOM language, one should be careful to fully understand the differences between (approximate or exact) solutions to the two EOMs discussed here.

Although we have now made the points which motivated this note, one important task which, because of the author's lack of insight, is left unresolved is an analysis of the consequences and possible utility of the flexibility remaining in those $O_L^\dagger(N, M)$ which obey Eq. (2) (and perhaps $O_L(N, M)\psi_0^{(M)} = 0$). Is this flexibility a useful attribute which would tend to favor use of the *function* EOM [Eq. (21)], or is knowledge that the desired excitation operator is uniquely determined, as in Eq. (4), a strong argument in favor of the operator EOM [Eq. (4)]? This is an important question which cannot be answered by speculation or by wishful thinking; one must directly address the meaning of the nonuniqueness of solutions to Eq. (2).

Acknowledgment

The author was an Alfred P. Sloan Fellow 1973–77 and a Camille and Henry Dreyfus Fellow 1976–81.

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Received November 3, 1976
Revised January 3, 1977