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Force on an atom in an electrostatic field: Feynman-Hellmann theorem and oscillator strengths

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The force on a free atom or ion in a uniform electrostatic field is considered in the framework of the Feynman-Hellmann theorem. The contributions to the force from excited states are shown to be given directly by the "oscillator strengths" between these states and the occupied states in the atom or ion. Force calculations for atoms in molecules and solids are discussed in the light of these results. In the case of current carrying solids, the Feynman-Hellmann theorem is not applicable, yet the force expression for an ion in the solid retains the Feynman-Hellmann form. Because of this distinction, arguments based on local neutrality of an ion in a solid are relevant for an isolated solid but not for a current carrying solid. A previously derived sum rule for the force on the ions of a conducting solid is shown to be a statement of the oscillator-strength sum rule.

I. INTRODUCTION

The motion of atoms in external electrostatic fields is of interest from both a fundamental and technological point of view. Some of this interest centers around the migration of impurity atoms in a metal in the presence of an external electric field, which is the phenomenon known as electromigration.[1] Other related phenomena include ionic transport in solid or liquid electrolytes[2,3] and molecular transport in ionic liquids.[3]

In treating some of these phenomena, one can attempt to describe the motion of the atom of interest by first calculating a force on the atom, or more precisely, on the nucleus of the atom. According to this picture, known as the Born-Oppenheimer approximation,[4] the nucleus is considered to be a classical particle while the electrons are treated fully quantum mechanically. The calculation of the force on the nucleus is therefore still a quantum-mechanical problem because the response of the electrons to the external field is required.

In general, a quantum-mechanical calculation of the force on a nucleus in a solid or liquid is a very difficult task because the quantum states of the system are known only very imperfectly. Both continuum and bound states must be considered. The necessity of including all the eigenstates is best seen in a somewhat related but much simpler problem, namely, the computation of the electrostatic force on a free atom. In this case we even know the answer; the net force should be zero, which follows either from classical arguments or from Ehrenfest's theorem.[5] However, the relative importance of the various energy states is not commonly recognized unless the problem is looked at from a microscopic point of view.

Our purpose in this paper is as follows: First, to illustrate the use of the Feynman-Hellman theorem[6] in calculating the electrostatic force on a free atom or ion. Second, to show that the relative contribution from the various states is precisely given by the so-called oscillator strengths associated with those states. (The "oscillator strength" is well known by its critical role in theories of optical transitions.[7,8]) Third, to critically discuss the more difficult problem of the force on an atom in a solid that is subjected to an external field.

II. FEYNMAN-HELLMANN THEOREM IN AN EXTERNAL FIELD

The Feynman-Hellmann theorem[6] expresses the force on a nucleus in terms of the electron density in the system. The force is shown to be precisely the electrostatic force that would be exerted on the nucleus by a classical charge distribution equal to the actual quantum mechanical charge distribution in the system.

If the nucleus of interest has Z_p protons and the actual electron density in the system is $n(\vec{r})$, the force on this nucleus in an external electrostatic field $\vec{E}$ can be written in the Feynman-Hellmann form

$$\vec{F}=Z_p e\vec{E}+\int n(\vec{r})\vec{\nabla}V(\vec{r})d^3r+\vec{F}_{\text{nuc}}\,, \tag{1}$$

where e is the charge of a proton and $V(r)=-Z_p e^2/|\vec{r}|$ is the electron-nucleus interaction. The nucleus is taken to be at the origin and the integral is over all space. The first term in Eq. (1) is the direct force exerted by the external field (or external charges) on the nucleus. The second term is the force exerted by the electrons in the system on the nucleus. The third term, $\vec{F}_{\text{nuc}}$, is the electrostatic force on the nucleus due to all other nuclei in the system. Equation (1) is exact provided that $n(\vec{r})$ is the exact quantum mechanical electron density in the presence of the field.

Since we shall be concerned with weak electric fields we need only calculate Eq. (1) to terms linear in $\vec{E}$. To this order we denote the net force by $\delta\vec{F}$ and write

$$\delta\vec{F} = Z_p e\vec{E} + \delta\vec{F}^{el}, \tag{2}$$

where $\delta\vec{F}^{el}$ is the linear part of the force exerted by the polarized electrons on the nucleus. Clearly

$$\delta\vec{F}^{el} = \int \delta n(\vec{r})\nabla V(\vec{r})d^3r, \tag{3}$$

where $\delta n(\vec{r})$ is that part of the electron density $n(\vec{r})$ which is linear in $\vec{E}$. (We are tacitly assuming that the surrounding nuclei do not appreciably move in the presence of the field $\vec{E}$. Otherwise we should also include in $\delta\vec{F}$ any changes in $\vec{F}_{nuc}$ due to the changed positions of the nuclei surrounding the nucleus of interest.)

In Sec. III we evaluate Eq. (3) for the case of an isolated atom in a weak applied field, and explicitly display contributions from the various unperturbed states involved in $\delta n(\vec{r})$.

III. CONNECTION BETWEEN FORCE AND OSCILLATOR STRENGTH

For simplicity we shall calculate the force for a one-electron system. Denoting the total Hamiltonian by $\mathcal{H}$, we have

$$\mathcal{H} = H + exE, \tag{4}$$

where H is the Hamiltonian in the absence of the field. It has the form

$$H = p^2/2m + V(\vec{r}), \tag{5}$$

where $\vec{p}$ is the electron momentum and m is the electron mass. The electric field has been taken to lie along the x direction. Strictly speaking, the forms (4) and (5) are valid only for a one-electron problem. However, these expressions can approximate a many-electron problem in an independent electron picture where the exchange interaction may be treated as a local potential.[9] In any case, the result we shall obtain can be rigorously established for the exact many-body problem, although the derivation is algebraically more cumbersome. The many-body derivation is outlined later.

To obtain $\delta n(\vec{r})$ we can use standard first-order perturbation theory for the wave function of a particle initially in state ψ_0 before the electrostatic perturbation xeE is turned on. The result is[10]

$$\delta n(\vec{r}) = \sum_n{}' \frac{\psi_n(\vec{r})\psi_0^*(\vec{r})x_{n0}eE}{\epsilon_0 - \epsilon_n} + \text{c.c.}, \tag{6}$$

where the sum is over all excited states ψ_n of the Hamiltonian H. (The prime on the sum indicates that $n=0$ is excluded.) ϵ_0 and ϵ_n are the energies of the unperturbed states ψ_0 and ψ_n, respectively. x_{n0} is the matrix element $\int\psi_n^*(\vec{r})x\psi_0(\vec{r})d^3r$.

Substituting (6) into (3) we obtain for the force

$$\delta\vec{F}^{el} = eE\sum_n{}' \frac{(\nabla V)_{0n}x_{n0}}{\epsilon_0 - \epsilon_n} + \text{c.c.}. \tag{7}$$

To simplify (7) we use the fact that $\nabla V = i\hbar^{-1}[\vec{p}, V]$, which follows from the representation of momentum as $\vec{p} = -i\hbar\partial/\partial\vec{r}$. Further note that $[\vec{p}, V] = [\vec{p}, H]$ and hence $(\nabla V)_{0n} = i\hbar^{-1}\vec{p}_{0n}(\epsilon_n - \epsilon_0)$. The x component of the force is thus

$$\delta F_x^{el} = -\frac{ieE}{\hbar}\sum_n{}' (p_x)_{0n}x_{n0} + \text{c.c.}, \tag{8}$$

where p_x is the x component of the momentum. By writing the matrix elements $(p_x)_{n0}$ in terms of x_{n0} using the commutation rule $p_x = im\hbar^{-1}[H, x]$, Eq. (8) becomes

$$\delta F_x^{el} = -eE\sum_n f_{n0}, \tag{9}$$

where

$$f_{n0} = (2m/\hbar^2)(\epsilon_n - \epsilon_0)|x_{n0}|^2 \tag{10}$$

is precisely the oscillator strength for the transition $0 \to n$.[7,8] The "oscillator strengths" satisfy the Thomas-Reiche-Kuhn sum rule[7,8]

$$\sum_n f_{n0} = 1, \tag{11}$$

which leads to the expected result $\delta F_x^{el} = -eE$. The sum rule (11) can be immediately obtained from Eq. (8) by noting that if we sum over all states

$$\sum_n (p_x)_{0n}x_{n0} - \text{c.c.} = [p_x, x]_{00} = -i\hbar.$$

The sum in (8) can be taken over all states since $x_{00} = 0$, the bound state ψ_0 having definite parity.

In the above we have assumed only the state ψ_0 is initially occupied. If there are N states independently occupied then

$$\delta F_x^{el} = -eE\sum_{l=1}^{N}\sum_n f_{nl}, \tag{12}$$

where the originally occupied states are labeled by l. The sum rule (11) holds for the state 0 replaced by any state l so that Eq. (12) gives a total force $\delta F_x^{el} = -NeE$, as expected for an N-electron atom.

To derive the general many-body form of the result (12) we abandon the one-electron approximation and include the electron-electron interaction U along with the electron-nucleus interaction V in the Hamiltonian H of Eq. (5). The new derivation proceeds along the same lines given above, with the wave functions and charge density written in their many-body form. In generalizing the one-electron equations, the operator x should be replaced by X, which is the sum of the x coordinates of all the electrons in the system. In Eq. (7) we may replace ∇V by $i\hbar^{-1}[\vec{P}, V]$, where $\vec{P}$ is the sum of the electron momenta. Further, $[\vec{P}, V] = [\vec{P}, H]$ since $[\vec{P}, U] = 0$. We then arrive at the many-body generalization of (12), namely,

$$\delta F_x^{\mathrm{el}} = -eE \sum_{l,n} f_{nl}\rho_l \,, \tag{13}$$

where ρ_l is the probability of occupation of the many-body state l in the absence of the field ($\sum_l \rho_l = 1$). The sums in (13) are over all states n, l and the oscillator strength f_{nl} has the many-body form

$$f_{nl} = \frac{2m}{\hbar^2}\,(\epsilon_n - \epsilon_l)\,|X_{nl}|^2 \,, \tag{14}$$

where now ϵ_n and ϵ_l are the energies of the exact many-body states ψ_n and ψ_l, respectively. X_{nl} is the matrix element $\langle \psi_n | \sum_i x_i | \psi_l \rangle$, where the sum over i is over all N electrons in the system. For a many-electron system Eq. (13) is exact regardless of the details of electron screening. If a product wave function (independent electrons) is assumed, Eq. (13) reduces to Eq. (12).

IV. DISCUSSION

A. Force on an isolated atom

Equation (9) gives the electrostatic force on an isolated atom having an electron originally in state ψ_0. The expression shows that the contribution from an excited state ψ_n is precisely given by the "oscillator strength" f_{n0}. That is, the oscillator strength for a particular virtual-transition $o \to n$ gives the fraction of a charge contributed by the particular virtual transition in the screening of the nucleus in an external field. In the usual context where oscillator strengths occur, such as in polarizability and optical absorption,[7,8] the f_{nl} appear in sums with various weighting factors so there is no direct connection between the oscillator-strength sum and these properties. Here, however, the f_{nl} appear in the force expression without weighting factors.

The oscillator strengths can be explicitly evaluated for one-electron atoms.[8] For example, in the case of a hydrogen atom in its ground state the contribution to the sum (11) from the bound states is 0.565; from the continuum states it is 0.435.[11] This illustrates the importance of using all eigenstates, including the continuum states, in a microscopic evaluation of the force on an atom. For a hydrogen atom initially in an excited state, the contribution from the continuum spectrum may be somewhat smaller, e.g., for an electron in a $3d$ level[11] the transitions to the continuous spectrum contribute only $-0.1\ eE$ to the total force.

B. Force on an atom in an isolated molecule or solid

Equations (9), (12), or (13) are of limited usefulness in discussing forces on an isolated molecule or solid. These expressions would now apply only to the *total* force summed over all nuclei in the system. To see this, extend the derivation of Sec. III to the entire system by allowing $V(\vec{r})$ to be the *total* potential seen by an electron from *all* the ion centers in the system. This allows us to replace $[\vec{P}, V]$ by $[\vec{P}, H]$, which is the critical step in progressing to Eq. (8) and beyond. One then finds, either in a one-electron or many-electron picture, that the net force from the electrons on all nuclei in an isolated molecule or solid is exactly $-Ne\vec{E}$. just as in the case of an isolated atom or ion. Unfortunately, the force on one particular nucleus is not directly given by an expression such as (12) or (13). As we have pointed out, the development leading to these expressions comes to an abrupt halt if $V(\vec{r})$ is not the *total* potential from *all* the ion centers. Consequently, for the case of atoms in molecules or solids we are left with an expression like (7) which requires explicit evaluation of the matrix elements of ∇V and x to all excited states. There appears to be no possibility of using the oscillator-strength sum rule which led to $\delta\vec{F}^{\mathrm{el}} = -Ne\vec{E}$.

A more useful approach for isolated molecules and solids might be to start from the original force expression before the application of the Feynman-Hellmann theorem,[6] i.e.,

$$\vec{F} = -\frac{\partial \mathcal{E}}{\partial \vec{R}} \,, \tag{15}$$

where $\mathcal{E}$ is the energy in the presence of the external field and $\vec{R}$ is the coordinate of the nucleus in question. If Ψ is the exact (many-body) wave function in the presence of the field, then $\mathcal{E} = \langle \Psi | \mathcal{H} | \Psi \rangle$. Denoting by $\delta\mathcal{E}$ that part of $\mathcal{E}$ linear in the external field, standard first-order perturbation theory leads to

$$\delta\mathcal{E} = \int n_0(\vec{r})\vec{r} \cdot e\vec{E}\, d^3r \,, \tag{16}$$

where $n_0(\vec{r})$ is the exact electron density in the *absence* of the external field $\vec{E}$. The force $\delta\vec{F}^{\mathrm{el}}$ is given by $-\partial(\delta\mathcal{E})/\partial\vec{R}$.

Equations (15) and (16) imply that for any part of the density $n_0(\vec{r})$ which depends on $\vec{R}$ through the explicit form $f(\vec{r} - \vec{R})$, the force becomes

$$\delta\vec{F} = Q\vec{E}\,, \qquad (17)$$

where $Q = -e\int f(\vec{r})d^3r$ is the net electron charge associated with the nucleus at $\vec{R}$. The implication is that for ionic-like electron states which carry a given electron charge Q with the nucleus, the nucleus acts like an entity whose net charge is $Z_p e + Q$. Thus $\delta\vec{F} = 0$ if the nucleus-electron complex is locally neutral and *remains* locally neutral as the nuclear coordinate $\vec{R}$ is varied around its original position ($Q = -Z_p e$ in this case).

C. Force on an atom in a conducting solid

The conducting solid differs from the isolated solid in the implied boundary conditions for the system. The wave functions for the isolated system vanish at infinity. The conducting solid, however, supports a continual current into one boundary and out of the opposite boundary. These boundaries are really interfaces with the metal electrodes attached to the sample. Despite these different boundary conditions, there is no formal difference between theoretical descriptions of the isolated solid and the conducting solid in the quantum-mechanical linear-response theory, e.g., Kubo theory.[12] In either case one assumes a perturbation $e\vec{X}\cdot\vec{E}$ and calculates the system response using the unperturbed wave functions, just as in Sec. III. The boundary conditions enter only implicitly in the form of ψ_0 and ψ_n for each case.

Based on the work of Kohn and Luttinger[13] and on arguments presented elsewhere,[14] it appears correct to assume periodic boundary conditions and to identify the electric field $\vec{E}$ with the actual macroscopic field present in the solid. Here one is ignoring any polarization charges at the sample boundary and is treating the macroscopic field as an external field in the theory. This picture is invoked to avoid dealing with screening effects which are difficult to treat microscopically. A semiclassical discussion of boundary conditions in transport theory has been given by Landauer.[15]

An important consequence of the different boundary conditions implicit in conducting and isolated solids is that the Feynman-Hellmann theorem is no longer valid. The statement of the Feynman-Hellmann theorem is that Eqs. (1) and (15) are equivalent.[6] For conducting solids this theorem no longer is true, since vanishing wave functions at infinity are implicity assumed in the derivation of the theorem. Furthermore, the concept of force as an energy derivative [Eq. (15)] is not meaningful in a system where electrons are flowing in and out of the sample. A wave-packet picture is now more appropriate than the picture of an isolated system in a stationary eigenstate. Consequently Eqs. (15)–(17) are not relevant. On the other hand, Eq. (1) is relevant since it gives the force as the expectation value of the force operator ∇V and this is a meaningful concept in the wave-packet picture. As an example, consider a proton in an electron gas. Since the electrons give rise to local neutrality, Eq. (17) would predict no net force on the nucleus. This prediction is incorrect because Eq. (17) is not applicable, despite the fact that it has been implicitly assumed in the past for the electromigration problem.[16]

It is interesting that the electrostatic force expression (1) is still physically relevant although its connection with the energy derivative (15), and hence with the Feynman-Hellmann theorem, is broken. One should therefore avoid saying that Eq. (1) holds for the conducting solid because of the Feynman-Hellmann theorem. In the derivation of Eq. (1) for conducting solids[17-19] one writes $\vec{F} = \langle\Psi| -\partial H_T/\partial\vec{R}|\Psi\rangle$ where H_T is the total system Hamiltonian (including all electrons and ions) and Ψ is the total system wave function. [This expression follows from identifying $\vec{F}$ with the time rate of change of the expectation value of the ion's momentum $d\langle\Psi|\vec{\mathcal{P}}|\Psi\rangle/dt$ and expressing the latter as $(i\hbar)^{-1}\langle\Psi|[\vec{\mathcal{P}}, H_T]|\Psi\rangle$]. Assuming the ions to be heavy classical particles allows us to use very localized wave functions for the ions. This permits the replacement of Ψ with only the electronic wave function, the latter being calculated for electrons in the external field and in the presence of the specified arrangement of ions. Equation (1) immediately follows. Thus Eq. (1) is established regardless of the fact that Eq. (15) is inapplicable.

Since Eq. (13) is derived from the still applicable Eq. (1), that equation holds for the conducting solid as well as for the isolated systems discussed earlier. The net force $\delta\vec{F}$ summed over all nuclei is again $-Ne\vec{E}$. This sum rule is a general result which has been already derived by workers in electromigration using the Kubo formalism.[20,21] We now see that this result is just a statement of the oscillator-strength sum rule.

As an example of the use of the sum rule consider the case of N_i impurities randomly distributed in an electron gas. Since the impurities share the force equally (on an ensemble average), the force on one impurity is $-Ne\vec{E}/N_i$. Although this argument has been used before,[17] we wish to emphasize that it has been implicitly assumed that the system is an infinite system with no boundary polarization effects. Furthermore, the infinite geometry is taken to imply that the uniform positive background (jellium) which neutralizes the system does not absorb any net force from the electrons. If these conditions are not met, as for example in a finite geometry, the sum rule leads only to the uninteresting result that the total force on all the nuclei and the positive background equals $-Ne\vec{E}$.

Apart from this special case of N_i identical nuclei (and no other scatterers) in an electron gas, the general problem for the force on a nucleus in a conducting solid is exceedingly difficult. The external field gives rise to local polarization of the electrons (including bound states, if any) and electron current as well. As implied in our calculation of Sec. III, a proper evaluation,of the force requires a full calculation with both bound and continuum states taken into account. Various approaches have been used.[18] Among the more promising is a fully quantum-mechanical linear-response theory approach.[19] Thus far, however, only some approximate results have been obtained within this formalsim.[19,22] In the calculations thus far published, both bound and continuum states have not yet been explicitly taken into account.[23]

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[1] See, for example, H. B. Huntington in *Diffusion in Solids: Recent Developments*, edited by A. S. Nowick and J. J. Burton (Academic, New York, 1974), Chap. 6. More recent references may be found in the review by R. S. Sorbello in *Electro- and Thermo-Transport in Metals and Alloys*, edited by R. E. Hummel and H. B. Huntington (Metallurgical Society of AIME, New York, 1977).

[2] See, for example, Diffusion in Solids (Ref. 1), Chap. 8 and 9.

[3] See, for example, J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry* (Plenum, New York, 1970), and J. O'M. Bockris and S. U. Khan, *Quantum Electrochemistry* (Plenum, New York, 1979).

[4] See, for example, J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1963), Vol. 1.

[5] See, for example, L. I. Schiff, *Quantum Mechanics*, 3rd ed. (McGraw Hill, New York, 1955), pp. 28–30.

[6] R. P. Feynman, Phys. Rev. 56, 340 (1939). See also Ref. 4 and B. M. Deb, Rev. Mod. Phys. 45, 22 (1973).

[7] See, for example, H. A. Bethe and R. Jackiw, *Intermediate Quantum Mechanics*, 2nd ed. (Benjamin, New York, 1968), Chap. 11.

[8] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Plenum, New York, 1977).

[9] For one-electron descriptions of atoms see, for example, Ref. 8 or E. U. Condon and G. H. Shortley, *Theorv of Atomic Spectra* (Cambridge University Press, Cambridge, 1967). For one-electron descriptions of solid, see, for example, J. M. Ziman, *Principles in the Theory of Solids* (Cambridge University Press, Cambridge, 1972). In applying a one-electron description of a many-electron problem, note that the one-electron potential $V(\vec{r})$ should no longer be taken as the electron-nucleus interaction $-Z_p e^2/|\vec{r}|$. Rather, $V(\vec{r})$ should be considered as an effective potential energy seen by an electron, including both electron screening and exchange in approximate way.

[10] We assume that nondegenerate perturbation theory is applicable. In the special case of accidental degeneracy it may happen that states of different parity are degenerate and the perturbation theory expression is not valid since $x_{n0} \neq 0$ while $\epsilon_0 - \epsilon_n = 0$. However, our final result Eq. (9) holds for this case also. This can be seen by artificially adding a tiny perturbation $\lambda u(\vec{r})$ to H in order to remove the degeneracy. The derivation now proceeds to the result (9), where f_{n0} is proportional to the actual energy difference $\epsilon_n - \epsilon_0$ in the presence of $\lambda u(\vec{r})$. As $\lambda \to 0$, $\epsilon_n - \epsilon_0$ remains well-behaved and δF^{el} approaches the result originally obtained by nondegenerate perturbation theory. In the many-body case, the possibility of accidental degeneracy is customarily excluded from the outset because of the complicated nature of the interactions. Any effects due to the quasi-continuous distribution of ϵ_n for the many-body system do not affect the final result (13). The quasi-continuum distribution requires the addition of an infinitesimal imaginary part $i\eta$ in the denominator of the perturbation theory expression. The δ function which arises from this does not change result (13) since there is a factor of $\epsilon_n - \epsilon_0$ in Eq. (14), and this equals zero when the δ function is nonzero.

[11] Reference 8, p. 265.

[12] R. Kubo, J. Phys. Soc. Jpn. 12, 570 (1957).

[13] W. Kohn and J. M. Luttinger, Phys. Rev. 108, 590 (1957).

[14] R. S. Sorbello and B. Dasgupta, Phys. Rev. B 16, 5193 (1977). See Sec. II.

[15] R. Landauer, Phys. Rev. B 16, 4698 (1977). See also R. Landauer, Phys. Rev. B 14, 1474 (1976); IBM J. Res. Dev. 1, 223 (1957).

[16] Arguments based on assuming Eq. (17) is valid can be found in the references cited in Ref. (1). Such arguments have been confined to the so-called direct or electrostatic force in electromigration. (The electron-current contribution, the so-called wind force, is treated separately in these discussions.) The fact that the Feynman-Hellmann theorem does not apply for a current-carrying electron gas has also been noted by H. E. Rorschach (unpublished).

[17] R. S. Sorbello, Comments Solid State Phys. 6, 117 (1975).

[18] For discussion of these other approaches see Refs. 14, 15, and R. S. Sorbello, Ref. 1.

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[20] P. Kumar and R. S. Sorbello (unpublished).

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[22] L. J. Sham, Phys. Rev. B 12, 3142 (1975), W. L. Schaich, Phys. Rev. B 13, 3350 and 3360 (1976); 19, 620 (1979).

[23] Some discussion of bound states has been given by B. Bell (unpublished), using the formalism of J. M. Luttinger and W. Kohn, Phys. Rev. 109, 892 (1958). Additional discussion is in the paper by P. R. Rimbey and R. S. Sorbello (unpublished).