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Inequalities for Isothermal Linear Response

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Abstract

The inequality that Brown, Hornreich and Shtrikman (1968) reported for the magneto-electric susceptibility is shown to be valid quite generally for all isothermal linear response coefficients. Certain difficulties in the derivation are removed.

1. Introduction

In 1968 Brown, Hornreich and Shtrikman reported an inequality that stated that the square of the magneto-electric susceptibility of any material was less than or equal to the product of its paraelectric and paramagnetic susceptibilities. Their derivation contained two shortcomings: first, they did not obtain explicit expressions for these susceptibilities, and second, their derivation did not appear to be applicable to materials that contain degenerate energy levels because of divergent denominators in their expression for the free energy. This rather large class of materials includes all paramagnetic systems containing unpolarised local moments. In this paper it is shown how these shortcomings may be circumvented and that inequalities (15) and (16) may be obtained that are valid for *all* suitably defined isothermal linear response coefficients, not only magneto-electric ones.

2. Free Energy

Consider a system in thermal equilibrium at a constant temperature T to which a perturbation V is applied of the form:

$$V = -\sum_{s} O_s F_s \,, \tag{1}$$

where the F_s are small steady applied classical multipolar electric, magnetic or exchange fields which couple to quantum mechanical operators O_s of the system. As one particular example V might be given by

$$-\boldsymbol{p}.\boldsymbol{E} - \boldsymbol{m}.\boldsymbol{B} - 2\mu_B\, \boldsymbol{S}.\boldsymbol{B}_{ex} \,,$$

where $\boldsymbol{p}, \boldsymbol{m}$ $\{=\mu_{\rm B}(\boldsymbol{L}+2\boldsymbol{S})\}$ and $\boldsymbol{S}$ are the operators for the vector electric and magnetic dipole moments and the spin of the system. Here $\boldsymbol{E}$ and $\boldsymbol{B}$ are the applied electric and magnetic fields and $\boldsymbol{B}_{\rm ex}$ is a fictitious exchange field

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often useful in the treatment of magnetic systems. The F_s are the individual components of these fields.

As a result of the perturbation, the eigenvalues of the Hamiltonian $\mathcal{H}$ that describes the system are changed from E_i to $E_i{}'$ where, to second order in perturbation theory,

$$E_i{}' = E_i + \langle i|V|i\rangle - \sum_j{}' \frac{|\langle j|V|i\rangle|^2}{E_j - E_i}\,, \tag{2}$$

and the prime on the sum over j means that the $j = i$ term is to be omitted. It is assumed for the time being that the quantum states $|i\rangle$ of the unperturbed system are non-degenerate.

The change of the eigenvalues following the application of the fields F_s results in a change of the partition function $Z = \Sigma_i \exp(-\beta E_i{}')$, where $\beta = 1/kT$ and k is Boltzmann's constant. This in turn perturbs the Helmholtz free energy $F = -kT\ln Z$, where $F = E - TS$, S being the entropy and $E = \langle\mathcal{H}\rangle$ the internal energy, given by the thermal expectation value of the Hamiltonian operator. By expanding in powers of the small quantity V it follows that

$$F - F_0 = \langle V\rangle_0 - \tfrac{1}{2}\sum_i \sum_j{}' \frac{|V_{ji}|^2(p_i - p_j)}{E_j - E_i} - \frac{1}{2kT}\langle(V_{ii} - \langle V\rangle_0)^2\rangle_0\,, \tag{3}$$

where $V_{ji} = \langle j|V|i\rangle$, F_0 is the free energy of the unperturbed system, $p_i = \exp(-\beta E_i)/Z_0$, $Z_0 = \Sigma_i \exp(-\beta E_i)$ is the partition function of the unperturbed system, and the angle brackets with subscript 0 denote $\Sigma_i\, p_i$, the ensemble average in the unperturbed state. Angle brackets without this subscript indicate the ensemble average in the perturbed state. Lifshitz and Pitaevskii (1980) attribute the above result to R. E. Peierls. An important feature of (3) is that the change in free energy that is of second order in the perturbation is negative-definite (≤ 0) because $p_i > p_j$ if $E_j > E_i$. The first-order term, given in our case by $-\Sigma_s F_s \langle O_s\rangle_0$, may be of either sign. An assumption implicit in the derivation is that the magnitude of the energy perturbation per particle is much less than kT.

The last term in (3) may be expressed as

$$\langle V\rangle_0^2/2kT - \sum_i \exp(-\beta E_i)\,\langle i|V|i\rangle\,\langle i|V|i\rangle/2kTZ_0.$$

Because of the denominator, the form of the second term on the right-hand side of (3) is not defined when the states i and j are degenerate; unpolarised magnetic materials will possess such states. To circumvent this difficulty, the limit

$$(\mathrm{e}^{-\beta E_i} - \mathrm{e}^{-\beta E_j})/(E_j - E_i) \;\to\; \beta\mathrm{e}^{-\beta E_i}$$

must be taken, and then these degenerate terms, together with the last term of (3), result in the degenerate parts of the second term of (3) being summed over *all* j with $E_j = E_i$. In addition, for the non-degenerate terms, the two terms with p_i and p_j are equal, so (3) may be expressed in the following alternative form, in which the terms involving degenerate and non-degenerate states have been separated and the divergent denominators are absent:

$$F - F_0 = \langle V \rangle_0 - \tfrac{1}{2} Q + \langle V \rangle_0^2 / 2kT \,, \tag{4}$$

with

$$Q = \frac{1}{Z_0} \sum_i \mathrm{e}^{-\beta E_i} \sum_j |V_{ji}|^2 \{\delta_{E_j,E_i}/kT + 2(1-\delta_{E_j,E_i})/(E_j - E_i)\} \,. \tag{5}$$

The purpose of the Kronecker delta is to indicate that only terms with $E_j = E_i$ are to be included in the first (Curie) term of (5) and only terms with $E_j \neq E_i$ in the second (the Van Vleck term). The quantity Q is real and positive-definite, because $\exp(-\beta E_i)$ is greater than $\exp(-\beta E_j)$ if $E_j > E_i$. It also follows that $Q \geq \langle V \rangle_0^2 / kT$ if the second-order free energy is to be negative-definite (see the Appendix). The two equations above may also be obtained from the first three terms of the expansion of the expression:

$$\frac{Z}{Z_0} = \mathcal{T} \Big\langle \exp\Big(-2\pi \int_0^{\beta h/2\pi} V(\tau)\, \mathrm{d}\tau / h \Big) \Big\rangle_0 \,,$$

where $V(\tau)$ is in the Heisenberg picture with imaginary time $\tau = \mathrm{i}t$ and $\mathcal{T}$ is an operator that orders the arguments of the terms in the expansion of the exponential.

3. Susceptibilities

It is useful to consider an isothermal susceptibility R_{rs} defined by

$$\langle O_r \rangle = \langle O_r \rangle_0 + \sum_s R_{rs} F_s \,. \tag{6}$$

The explicit form of this susceptibility may be obtained by calculating $\langle O_r \rangle$ by perturbation theory (Stewart 1993*a*). A less direct but shorter derivation makes use of a standard result of quantum statistical mechanics (Lifshitz and Pitaevskii 1980) that the change $\mathrm{d}F$ in free energy resulting from changes in external parameters and temperature is given by

$$\mathrm{d}F = -S\,\mathrm{d}T + \sum_i \langle \partial \mathcal{H} / \partial \lambda_i \rangle \, \mathrm{d}\lambda_i \,, \tag{7}$$

where the λ_i are external parameters such as the volume or the fields F_s that determine the energy eigenvalues of the quantum system. In the notation used here this gives

$$\mathrm{d}F = -S\,\mathrm{d}T - \sum_s \langle O_s \rangle \mathrm{d}F_s \,,$$

or for the example given previously,

$$\mathrm{d}F = -S\,\mathrm{d}T - \boldsymbol{p}.\mathrm{d}\boldsymbol{E} - \boldsymbol{m}.\mathrm{d}\boldsymbol{B} - 2\mu_{\mathrm{B}}\,\boldsymbol{S}.\mathrm{d}\boldsymbol{B}_{\mathrm{ex}}\,.$$

Hence $\langle O_r \rangle = -(\partial F/\partial F_r)|_T$. The next step is to substitute the explicit form of the perturbation (1) into (5) and, noting that F_r occurs twice in the second-order part of (5), differentiation with respect to F_r of that equation leads to

$$R_{rs} = \chi_{rs} - \langle O_r \rangle_0 \langle O_s \rangle_0 / kT\,, \tag{8}$$

where

$$\chi_{rs} = \frac{1}{Z_0}\sum_i \mathrm{e}^{-\beta E_i} \sum_j \{\delta_{E_j,E_i}/kT + 2(1-\delta_{E_j,E_i})/(E_j - E_i)\} \times \mathrm{Re}\{\langle i|O_r|j\rangle \langle j|O_s|i\rangle\}\,. \tag{9}$$

It can be seen from inspection that χ_{rs} is real, that $\chi_{sr} = \chi_{rs}$, and that $\chi_{rr} \geq 0$. The second term on the right-hand side of (8) is zero when the system is initially unpolarised with $<O_r>_0$ or $<O_s>_0$ equal to zero. Equation (9) may also be derived from the time integral of the Kubo (1957) formula

$$\chi_{rs}(t, t') = \frac{2\pi\,\mathrm{i}}{h} \langle [O_r(t), O_s(t')] \rangle_0\, \theta(t - t')\,,$$

where the square brackets denote a commutator, the operators are in the Heisenberg picture and the function $\theta(x) = 1$ for $x > 0$ and 0 otherwise.

At zero temperature the system is in its (non-degenerate) ground state $|0\rangle$, so the Kronecker delta gives zero and

$$\chi_{rs} = 2\sum_j{}' \frac{\mathrm{Re}\{\langle 0|O_r|j\rangle \langle j|O_s|0\rangle\}}{E_j - E_0}\,. \tag{10}$$

Since the condition that the energy perturbation is much less than kT is not satisfied at zero temperature, the calculation needs to be carried out in terms of the perturbation of the ground-state energy and wavefunction. This leads to (10) but $R_{rs} = \chi_{rs}$ instead of (8). Because the ground-state is non-degenerate χ_{rr} is again positive-definite. At temperatures much larger than the separation between energy levels (assumed finite and N in number), both terms of (9) may be expanded in powers of $1/T$ to give

$$\chi_{rs} = \sum_i \sum_j Re\{\langle i|O_r|j\rangle \langle j|O_s|i\rangle\}/NkT\,, \tag{11}$$

or, by closure, assuming that the $|i\rangle$ form a complete set of states $\chi_{rs} = \mathrm{Trace}\{O_r\, O_s\}/NkT$, or $\chi_{rs} = \langle O_r\, O_s\rangle_0/kT$, where the correlation function is evaluated in the high-temperature limit. Hence, for example, the Curie constant of a paramagnetic ion becomes equal to the free-ion value at temperatures much greater than the crystal field splitting, but not so large as to cause thermal population of multiplet levels above the ground state.

4. Inequalities

By substituting (8), (9) and (1) into (4) and (5), it follows that the change in free energy may be expressed as

$$F - F_0 = -\sum_s F_s \langle O_s \rangle_0 - \tfrac{1}{2} \sum_r \sum_s F_r\, F_s\, R_{rs}\,, \tag{12}$$

with $R_{rs} = -(\partial^2 F/\partial F_r\, \partial F_s)\,|_T$. Since the second-order free energy in (12) is required to be negative-definite for all values of the applied fields, it follows first, by setting all the fields except r to be zero, that $R_{rr} \geq 0$ or (see the Appendix)

$$\chi_{rr} \geq \langle O_r \rangle_0^2 / kT\,. \tag{13}$$

At zero temperature the relation is $\chi_{rr} \geq 0$. Second, if all the fields are set to zero except for the pair F_r and F_s, the second-order free energy becomes the negative of $(F_s^2\, R_{ss} + F_r^2\, R_{rr} + 2F_s\, F_r\, R_{rs})$, which may be written in the algebraically identical form

$$\left(\sqrt{R_{rr}}\, F_r + \frac{R_{rs}}{\sqrt{R_{rr}}}\, F_s\right)^2 + F_s^2\,(R_{ss} - R_{rs}^2/R_{rr})\,.$$

For the free energy to be negative-definite, it follows that $R_{ss}\, R_{rr} \geq R_{rs}^2$ for all pairs of r, s. By substituting (8) into this relation we obtain

$$(\chi_{rr}\, \chi_{ss} - \chi_{rs}^2)(\chi_{ss} - \langle O_s \rangle_0^2/kT) \geq \left(\sqrt{\chi_{ss}} \langle O_r \rangle_0 - \frac{\chi_{rs}}{\sqrt{\chi_{ss}}}\, \langle O_s \rangle_0\right)^2 \chi_{ss}/kT\,. \tag{14}$$

Because the right-hand side is greater than zero, and by using (13), we finally get the inequality

$$\chi_{rr}\, \chi_{ss} \geq \chi_{rs}^2\,. \tag{15}$$

By considering more than two fields to have nonzero values the theory of quadratic forms leads to relations of the type (Perlis 1952):

$$\mathrm{Det} \begin{bmatrix} R_{rr} & R_{rs} & R_{rt} \\ R_{rs} & R_{ss} & R_{st} \\ R_{rt} & R_{st} & R_{tt} \end{bmatrix} \geq 0\,,$$

where Det indicates the determinant of the matrix, or

$$R_{ss}\, R_{rr}\, R_{tt} + 2R_{rs}\, R_{rt}\, R_{st} \geq 0\,, \tag{16}$$

and so forth.

The relation (15) may also be obtained by direct algebraic manipulation of (9), but the derivation given above is shorter and more physically instructive. There are several situations as well as the magneto-electric effect (Brown *et al.* 1968) in which the inequalities may be useful. For example, they apply to the individual components of the paraelectric and paramagnetic susceptibility tensors of crystals. When these tensors are referred to their principal axes, the off-diagonal components are zero (Nye 1957) and so (15) and (16) are satisfied trivially, but for crystals of low symmetry whose principal axes are not known *a priori*, these relations provide restrictions upon the measured components. Quite generally they apply to *any* response to *any* perturbation that may be expressed in the form of (1). Another use is to demonstrate that the paramagnetic susceptibility of a complex magnetic system, when expressed in terms of its component susceptibilities and properly defined inter-lattice exchange interactions, remains positive-definite (Stewart 1993*b*).

5. Diamagnetism

The arguments that have been used so far in this discussion apply only to perturbations that are linear in the applied fields. They do not apply, for example, to diamagnetic effects, whose Hamiltonian is quadratic in field, and so (13) does not constrain the diamagnetic susceptibility to be positive. The perturbing Hamiltonian for diamagnetism, $e^2\boldsymbol{A}^2/2m$ with $\boldsymbol{B}=\nabla\times\boldsymbol{A}$ where $\boldsymbol{A}$ is the electromagnetic vector potential, gives rise via the first term on the right-hand side of (3) to a change in free energy that is *positive*-definite. The atomic diamagnetic susceptibility tensor, defined to be $\chi^{\mathrm{D}}_{rs}=-(\partial^2F/\partial B_r\,\partial B_s)\,|_T$, is obtained with $\boldsymbol{A}=\boldsymbol{B}\times\boldsymbol{r}/2$, appropriate for a uniform magnetic field $\boldsymbol{B}$, to be

$$\chi^{\mathrm{D}}_{rs}=-\frac{e^2}{4m}\left\langle\begin{bmatrix} y^2+z^2 & -xy & -xz\\ -xy & z^2+x^2 & -yz\\ -xz & -yz & x^2+y^2\end{bmatrix}\right\rangle_0. \tag{17}$$

The free energy change is therefore also given by $-\frac{1}{2}\Sigma_r\,\Sigma_s\,B_r\,B_s\,\chi^{\mathrm{D}}_{rs}$. Consequently the total free energy change resulting from the application of a magnetic field to such a system is $-\frac{1}{2}\Sigma_r\,\Sigma_s\,B_r\,B_s\,(\chi^{\mathrm{D}}_{rs}+\mathrm{R}_{rs})$, where the first (diamagnetic) term in this expression is associated with the first term on the right-hand side of (3) and the second (paramagnetic) term is associated with the last two terms of that equation.

The atomic diamagnetic susceptibility tensor must satisfy the inequalities (15) and (16) to make the free energy change *positive*-definite. We demonstrate that the elements of this tensor have the required properties. Consider, for example, $\chi_{xx}\,\chi_{yy}-\chi^2_{xy}$. From (17) this is proportional to $(\langle z^2\rangle\,\langle r^2\rangle+\langle x^2\rangle\langle y^2\rangle-\langle xy\rangle^2)$. But $\langle x^2\rangle\,\langle y^2\rangle\geq\langle xy\rangle^2$ by the Schwarz–Cauchy inequality (Hardy *et al.* 1952), so therefore inequality (15) is satisfied. By expanding the positive quantities $\langle(x\pm y)^2\rangle$ for the pairs of arguments (x,y), (y,z) and (z,x), and by multiplying them together, it can be shown that inequality (16) is satisfied too. However, the elements of the *sum* of the paramagnetic and atomic diamagnetic susceptibility tensors, which would be measured in an experiment, need not satisfy these inequalities.

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Appendix

To demonstrate explicitly that $Q \geq \langle V\rangle_0^2/kT$, it suffices to show that

$$\frac{1}{Z_0}\sum_i \mathrm{e}^{-\beta E_i} \sum_j^{E_j=E_i} |V_{ji}|^2 \geq \langle V_0\rangle^2 . \tag{A1}$$

Consider the positive quantity:

$$\frac{1}{Z_0}\sum_i \mathrm{e}^{-\beta E_i}[\langle i|V|i\rangle - \langle V_0\rangle]^2 . \tag{A2}$$

By multiplying out the square bracket it follows that

$$\frac{1}{Z_0}\sum_i \mathrm{e}^{-\beta E_i}\langle i|V|i\rangle^2 \geq \left(\frac{1}{Z_0}\sum_i \mathrm{e}^{-\beta E_i}\langle i|V|i\rangle\right)^2 = \langle V\rangle_0^2 . \tag{A3}$$

Since (A1) contains the positive squares of the off-diagonal elements, as well as the diagonal elements, (A1) is true *a fortiori*. An identical argument is used to prove that $\chi_{rr} \geq \langle O_r\rangle_0^2/kT$.

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