

Failure of the Electronic Quasiparticle Picture for Nuclear Spin Relaxation in Metals

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(Received 17 July 1963)

This paper investigates the range of validity of the quasiparticle picture by calculation of the temperature dependence of the nuclear spin relaxation time T_1 . According to the simplest application of the quasiparticle picture, the electron-phonon interaction should produce a considerable deviation from the weak coupling law, $T_1 T = \text{constant}$. This deviation is not observed experimentally. Moreover, a more modern approach, based upon field theoretic techniques, predicts the constancy of $T_1 T$ and hence restores the agreement between theory and experiment. Therefore, it is argued that the quasiparticle picture is a most inappropriate description of the effects of the electron-phonon interaction in metals.

INTRODUCTION

THE authors of recent papers on tunneling in superconducting¹ and normal² metals have indicated that the simplest version of the quasiparticle picture gives an incorrect description of metallic properties. In particular, this picture grossly falsifies the effects of the electron-phonon interaction upon the tunneling rate.

This paper explicitly demonstrates the failure of the simple quasiparticle picture for the calculation of the nuclear spin-lattice relaxation time T_1 . Both experiment³⁻⁸ and the more exact theory presented here indicate that the product of T_1 and the temperature T should be independent of temperature. However, the quasiparticle picture predicts a completely spurious temperature dependence of the product $T_1 T$.

[*Note added in proof.* The reader should notice that we are here objecting to the simplest version of the quasiparticle picture and not to the more sophisticated version derived, for example, by Nozières (see Ref. 13, below) with the aid of field theoretic techniques. This latter approach leads to results which are essentially identical to those presented below.]

In order to make our point in the simplest possible fashion, we neglect all effects of band structure and the Coulomb interaction between particles. This neglect is justified because the characteristic energy for a Coulomb interaction in a metal is of the order a few electron volts which corresponds to temperatures of more than 20 000°K. No important temperature dependence will be produced by the Coulomb interaction until the temperature reaches these impossibly high levels.

On the other hand, the characteristic temperature for the electron-phonon interaction is the Debye tempera-

ture which is of the order of 300°K. Therefore, this interaction must be included in any calculation of the temperature dependence of T_1 .

To calculate T_1 , we follow the conventional⁹ viewpoint that nuclear spin relaxation is produced by processes in which an electron scatters from a nucleus and thus changes the nuclear spin. This interaction is represented by the interaction Hamiltonian

$$V = (8\pi/3)\gamma_e\gamma_n\mathbf{I}\cdot\mathbf{S}(\mathbf{r}), \quad (1)$$

where \mathbf{I} is the nuclear spin vector and $\mathbf{S}(\mathbf{r})$ is the electronic spin density at the nucleus. A simple golden-rule calculation of the transition rate from the nuclear state m (energy E_m) to the state n (energy E_n) gives the transition rate as:

$$W_{mn} = C_{mn} \int \frac{d^3k}{(2\pi)^3} \int \frac{d\omega}{2\pi} \int \frac{d^3k'}{(2\pi)^3} \times \int \frac{d\omega'}{2\pi} G^<(k,\omega)G^>(k',\omega')\delta(E_m+\omega-E_n-\omega'). \quad (2)$$

This result is derived in Appendix A.

The important factors in the transition rate are $G^<(k,\omega)$ and $G^>(k',\omega')$. They are, respectively, the density of electrons (of one spin) with momentum k and energy ω and the density of states available to an electron with momentum k' and energy ω' . $G^>(k',\omega')$ can also be considered to be a density of holes.¹⁰ The factor C_{mn} contains the nuclear matrix elements and since it is independent of temperature it is irrelevant to our present considerations. Except for this factor, Eq. (2) contains the statement that the transition rate is proportional to the initial density of electrons, the final density of states, and an energy conserving delta function.

Since the nuclear energy difference is quite small, we neglect it in all our further considerations. In this way,

⁹ C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963), pp. 121-126. As in this reference, γ_e and γ_n are the gyromagnetic ratios of the nucleus and electron spin. We differ from this reference in using units in which $\hbar=1$.

¹⁰ See Ref. 2 or L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962), Chap. 2 for a discussion of the meaning of $G^>$ and $G^<$.

* This research was supported in part by the U. S. Army Research Office, Durham, North Carolina.

¹ J. R. Schrieffer, D. J. Scalapino, and J. W. Wilkins, *Phys. Rev. Letters* **10**, 336 (1963).

² Leo P. Kadanoff, *Notes from 1963 Ravello Spring School of Theoretical Physics* (W. A. Benjamin, Inc., New York, to be published).

³ J. J. Spokas and C. P. Slichter, *Phys. Rev.* **113**, 1462 (1959).

⁴ K. Asayama and J. Itoh, *J. Phys. Soc. Japan* **17**, 1065 (1962).

⁵ A. G. Anderson and A. G. Redfield, *Phys. Rev.* **116**, 583 (1963).

⁶ D. F. Holcomb and R. E. Norberg, *Phys. Rev.* **98**, 1074 (1955).

⁷ A. G. Redfield, *Phys. Rev.* **101**, 67 (1956).

⁸ L. C. Hebel and C. P. Slichter, *Phys. Rev.* **113**, 1502 (1959).

we find that the only temperature dependent term in W_{mn} is the common factor

$$\int \frac{d^3k}{(2\pi)^3} \int \frac{d^3k'}{(2\pi)^3} \int \frac{d\omega}{2\pi} \times \int \frac{d\omega'}{2\pi} G^<(k,\omega) G^>(k',\omega') \delta(\omega-\omega'). \quad (3)$$

Since T_1 is inversely proportional to the transition rates, we are necessarily led to conclude that the factor (3) contains all the possible temperature dependence of T_1^{-1} . Thus, we write

$$T_1^{-1} = C \int \frac{d\omega}{(2\pi)^2} \int \frac{d^3k}{(2\pi)^3} \int \frac{d^3k'}{(2\pi)^3} G^<(k,\omega) G^>(k',\omega), \quad (4)$$

where the factor C is necessarily independent of temperature.

Because the system is in thermodynamic equilibrium, the density of states is related to the density of particles by the detailed balancing relation

$$G^<(k,\omega) = \exp(-\omega/k_B T) G^>(k,\omega), \quad (5)$$

where k_B is the Boltzmann constant. Equation (5) defines a condition for thermodynamic equilibrium for the case in which all the energies are measured relative to the Fermi energy. This condition is conveniently represented by writing $G^>$ and $G^<$ in terms of the spectral weight function $A(k,\omega)$ as

$$\begin{aligned} G^<(k,\omega) &= f(\omega) A(k,\omega) \\ G^>(k,\omega) &= [1-f(\omega)] A(k,\omega), \end{aligned} \quad (6)$$

where

$$f(\omega) = [\exp(\omega/k_B T) + 1]^{-1}. \quad (7)$$

Equation (6) is convenient mainly because $A(k,\omega)$ satisfies the simple sum rule

$$\int \frac{d\omega}{2\pi} A(k,\omega) = 1, \quad (8)$$

which expresses the completeness of the set of states used in calculating $G^>$ and $G^<$.

To obtain a convenient expression for T_1^{-1} , we substitute (6) into (4) and employ the relationship

$$f(\omega)[1-f(\omega)] = -k_B T [\partial f(\omega)/\partial \omega]$$

to write (4) as

$$\begin{aligned} (T_1 T)^{-1} &= -C k_B \int \frac{d^3k}{(2\pi)^3} \int \frac{d^3k'}{(2\pi)^3} \\ &\times \int \frac{d\omega}{(2\pi)^2} A(k,\omega) A(k',\omega) \frac{\partial f(\omega)}{\partial \omega}. \end{aligned} \quad (9)$$

Finally, we notice that the factor $\partial f/\partial \omega$ is sharply

peaked near $\omega=0$. Therefore, only particles with energies very close to the Fermi energy contribute appreciably to the scatterings which define T_1 . Since the electron-phonon interaction produces shifts in the single-particle energies which are very much smaller than E_F , the predominant contributions to the integrals in (9) appear for $|\epsilon_k| \ll E_F$ and $|\epsilon_{k'}| \ll E_F$, where

$$\epsilon_k = (\hbar^2 k^2 / 2m) - E_F \quad (10)$$

is the kinetic energy measured relative to the Fermi energy. For this reason, we can make the replacement in (9)

$$\int \frac{d^3k}{(2\pi)^3} = \frac{m}{2\pi^2} \int_{-E_F}^{\infty} d\epsilon_k \approx \frac{m k_F}{2\pi^2} \int_{-\infty}^{\infty} d\epsilon_k, \quad (11)$$

where $k_F = (2mE_F)^{1/2}$ is the Fermi momentum.

In this way, we obtain our final expression for T_1^{-1}

$$\begin{aligned} (T_1 T)^{-1} &= -C k_B (N_0)^2 \int \frac{d\epsilon_k}{2\pi} \int \frac{d\epsilon_{k'}}{2\pi} \\ &\times \int d\omega A(k,\omega) A(k',\omega) \frac{\partial f(\omega)}{\partial \omega}. \end{aligned} \quad (12)$$

Here

$$N_0 = m k_F / 2\pi^2 \quad (13)$$

is the density of states in energy at the edge of the Fermi sea for a set of noninteracting fermions.

All effects of the electron-phonon interaction contained in the spectral weight functions $A(k,\omega)$. We now examine the behavior of T_1^{-1} by using (a) the free electron picture; (b) the quasiparticle picture; and (c) the theory of Migdal¹¹ to express $A(k,\omega)$.

FREE-ELECTRON PICTURE

For noninteracting electrons,

$$A(k,\omega) = 2\pi \delta(\omega - \epsilon_k). \quad (14)$$

Hence, Eq. (12) becomes

$$(T_1 T)^{-1} = -C k_B (N_0)^2 \int d\omega \frac{\partial f(\omega)}{\partial \omega}. \quad (15)$$

Since $f(\omega)$ goes to 1 at $\omega = -\infty$ and 0 at $\omega = +\infty$, the free-electron picture predicts

$$(T_1 T)^{-1} = C k_B (N_0)^2 \quad (16)$$

so that in this picture the product of T_1 and T is a constant, independent of temperature.

QUASIPARTICLE PICTURE

In the simplest version of the quasiparticle picture, the electrons are treated in exactly the same manner as free particles except that their energy-momentum rela-

¹¹ A. B. Migdal, Zh. Eksperim. i Teor. Fiz. 34, 1438 (1958) [translation: Soviet Phys.—JETP 7, 996 (1958)].

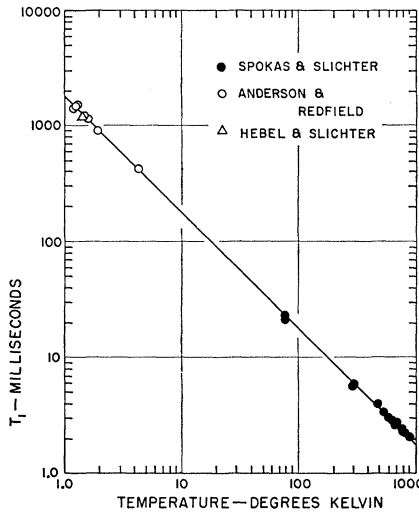


FIG. 1. T_1 versus T in Al. The line describes $T_1T = 1.85 \text{ sec} \cdot ^\circ\text{K}$. The maximum deviation of the data from this straight line is less than 5%.

tion is altered. Instead of writing (14), we write

$$A(k, \omega) = 2\pi\delta[\omega - E(k)], \quad (17)$$

where E is the true quasiparticle energy. We substitute (17) into (12) and find

$$(T_1T)^{-1} = -Ck_B \int_{-\infty}^{\infty} dE \left[N_0 \frac{d\epsilon(E)}{dE} \right]^2 \frac{\partial f(E)}{\partial E}. \quad (18)$$

Equation (18) may be described by saying that the zeroth-order density of states in energy N_0 is replaced by the "effective" density of states

$$N_0 [d\epsilon(E)/dE]. \quad (19)$$

In evaluating the effective density of states, we express the total energy E as the sum of kinetic energy ϵ and the interaction energy, $\Sigma(E)$.

$$E = \epsilon + \Sigma(E). \quad (20)$$

For the sake of convenience, we calculate the self-energy $\Sigma(E)$ for the case of an Einstein spectrum in which the phonon energy ω_e is constant and for constant electron-phonon matrix elements v . Then, a second-order perturbation theoretic calculation gives

$$\Sigma(E) = N_0 v^2 \mathcal{P} \int d\omega' \left[\frac{\bar{N} + f(\omega')}{E + \omega_e - \omega'} + \frac{\bar{N} + 1 - f(\omega')}{E - \omega_e - \omega'} \right], \quad (21)$$

where \mathcal{P} indicates that the integral is to be evaluated as a principal value integral. In (21),

$$\bar{N} = [\exp(\omega_e/k_B T) - 1]^{-1} \quad (22)$$

is the equilibrium number of phonons in any momentum state.

We examine T_1^{-1} in two limiting cases: the low-temperature limit in which $\omega_e \gg k_B T$ and the high-temperature limit in which $\omega_e \ll k_B T$.

First, in the limit of low temperature,

$$\bar{N} = 0$$

$$f(\omega) = 1 \text{ for } \omega < 0 \\ = 0 \text{ for } \omega > 0$$

and

$$\Sigma(E) = N_0 v^2 \mathcal{P} \int_{-\infty}^0 d\omega' \left[\frac{1}{E + \omega_e - \omega'} + \frac{1}{E - \omega_e + \omega'} \right].$$

The only contributions to (18) occur for very small E , for which

$$\Sigma(E) = -N_0 v^2 \int_{-\infty}^0 d\omega' \frac{2E}{(\omega_e - \omega')^2} \\ = -(2N_0 v^2 / \omega_e) E.$$

Thus, for small E and low temperatures

$$d\epsilon/dE = 1 + (2N_0 v^2 / \omega_e) \quad (23)$$

and (18) implies,

$$(T_1T)^{-1} = k_B C (N_0)^2 [1 + (2N_0 v^2 / \omega_e)]^2, \\ \text{for } k_B T \ll \omega_e. \quad (24)$$

On the other hand, for very high temperatures the $\Sigma(E)$ which appears in T_1^{-1} is mostly evaluated for very large E . Then the energy denominators which appear in $\Sigma(E)$ are so very large that $\Sigma(E)$ makes a negligible contribution to the effective density of states, $N_0 [1 - \partial\Sigma(E)/\partial E]$. In fact, a simple order of magnitude estimate gives

$$(T_1T)^{-1} = k_B C (N_0)^2 \left[1 + \mathcal{O} \left(\frac{\omega_e}{k_B T} \right)^2 \frac{N_0 v^2}{\omega_e} \right], \\ \text{for } k_B T \gg \omega_e. \quad (25)$$

Therefore, as one progresses from very low temperatures to very high temperatures, the quasiparticle picture predicts a change in the slope of the T_1^{-1} versus T curve by a factor

$$[1 + (2N_0 v^2 / \omega_e)]^2.$$

Figure 1 is a plot of experimental T_1^{-1} versus temperature curves for high magnetic field measurements in Al. Notice that within experimental error T_1T is constant. That is to say the experiment gives no evidence of the change in shape predicted by the quasiparticle picture.

And the predicted changes in slope are far from small. To estimate these, we use Morel and Anderson's¹² calculations of the quantity

$$\lambda = 2N_0 v^2 / \omega_e. \quad (26)$$

In Table I, we list values of λ and the characteristic

¹² P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962).

TABLE I. Comparison of theoretical and experimental values of the ratio $\{(T_1T \text{ for } T \gg \theta_D)/(T_1T \text{ for } T \ll \theta_D)\}$.

Material	θ_D (°K)	Experimental results						Theoretical results				
		High-temperature results			Low-temperature results			Quasiparticle theory		Present theory		
		Temperature range (°K)	T_1T (°K-sec)	Reference	Temperature range (°K)	T_1T (°K-sec)	Reference	Ratio T_1T for high T T_1T for low T	λ	Ratio T_1T for $T \gg \theta_D$ T_1T for $T \ll \theta_D$	Ratio T_1T for $T \gg \theta_D$ T_1T for $T \ll \theta_D$	
Al	375 ^a	400-930	1.85 ± 5%	3	1-4.2	1.80 ± 3%	5, 8	1.03 ± 6%	0.33 ^a	1.8	1	
Pb	96	200	0.022 ± 20%	4	4.2	0.029 ± 20%	4	0.8 ± 30%	0.40	2.0	1	
Na	160	250-450	4.8 ± 10% ^b	6	1-4.2	5.1 ± 6%	5	0.94 ± 10%	0.25	1.6	1	
Cu	343	300	1.06 ± 20%	7	1-4.2	1.27 ± 10%	5	0.84 ± 20%	0.20	1.4	1	
Li		300	45 ± 10% ^b	6	1-4.2	44 ± 5%	5	1.0 ± 10%			1	

^a Taken from Ref. 11.

^b In these cases, there is an appreciable magnetic field dependence of T_1T even for the high magnetic fields, 2000-9000 G, used in the experiment. This field dependence is probably indicative of an extra relaxation process due to impurities in the sample. The highest experimental value of T_1T is listed in the table because the extra relaxation process can only decrease T_1T . The error used is the observed variation of T_1T with magnetic field.

phonon temperature

$$\theta_D \sim \omega_e/k_B$$

which is also listed in this reference. This table also lists the quantity $(1+\lambda)^2$ which is the ratio

$$\frac{T_1T \text{ for } T \gg \theta_D}{T_1T \text{ for } T \ll \theta_D} = (1+\lambda)^2 \quad (27)$$

predicted by the quasiparticle theory.

Finally, the table gives experimental values of this ratio for the highest and lowest temperature regions which have been explored. Clearly, there is a real disagreement between the quasiparticle theory and experiment. The quasiparticle picture predicts a considerable temperature dependence for T_1T ; the experiments indicate no temperature dependence whatsoever for this quantity.

FIELD THEORETIC ANALYSIS

We can easily recover agreement between theory and experiment by using the results of Migdal,¹¹ which are believed to be an exact description (to order ω_e/E_F) of the electron-phonon interaction in normal metals. According to Migdal,

$$A(k, \omega) = \frac{\Gamma(\omega)}{[\omega - \epsilon_k - \Sigma(\omega)]^2 + [\Gamma(\omega)/2]^2}, \quad (28)$$

where $\Sigma(\omega)$ is the self-energy written down previously and $\Gamma(\omega)$ is the Kramers-Krönig transform of $\Sigma(\omega)$, i.e.,

$$\Sigma(\omega) = P \int \frac{d\omega'}{2\pi} \frac{\Gamma(\omega')}{\omega - \omega'}, \quad (29)$$

$$\Gamma(\omega) = 2\pi N v^2 \int d\omega' \{ \delta(\omega + \omega_e - \omega') [\bar{N} + f(\omega')] + \delta(\omega - \omega_e - \omega') [N + 1 - f(\omega')] \}. \quad (30)$$

Notice the relation of (28) to the quasiparticle picture. If $\Gamma(\omega)$, which is proportional to the inverse lifetime of

the single-particle state, is small, then $A(k, \omega)$ is sharply peaked for ω close to the quasiparticle energy $E(k)$. The failure of the quasiparticle picture is evidenced by the fact that even in the case of small $\Gamma(E)$, $A(p, \omega)$ is not $2\pi\delta[\omega - E(p)]$ as in Eq. (17). Instead,

$$A(p, \omega) = 2\pi\delta[\omega - \epsilon - \Sigma(\omega)] = \{2\pi/[1 - \partial\Sigma(E)/\partial E]\} \delta[\omega - E(\epsilon)]. \quad (31)$$

Thus, even when $\Gamma(E)$ is quite small, the simple quasiparticle picture is quite wrong.

The extra factor $(1 - \partial\Sigma/\partial E)^{-1}$ in Eq. (31) is the wave function renormalization which has been used by, for example, Nozières¹³ to refine the simple quasiparticle picture. With this refinement, the quasiparticle picture will be correct whenever $\Gamma(E)$ is small. However, we feel that it is simpler as well as more general to work directly with the Green's function formulation. In this formulation, we need not invoke any statement about $A(k, \omega)$ being sharply peaked in our calculation of T_1^{-1} . In particular, the results we are about to derive will be valid even when $\Gamma(\omega)$ is large.

To calculate T_1^{-1} , we notice that the $A(k, \omega)$ defined by (28) satisfies a sum rule, first derived by Migdal,¹¹

$$\int \frac{d\epsilon}{2\pi} A(k, \omega) = 1. \quad (32)$$

The sum rule (32) is derived by simply performing the ϵ integral of the expression (28). In contrast to Eq. (8), Eq. (32) is not exact. It is an approximate sum rule which is a consequence of the nature of the electron-phonon interaction.

To find T_1^{-1} , we now simply refer back to Eq. (12). We apply the sum rule (32) and find

$$(T_1T)^{-1} = -Ck_B(N_0)^2 \int d\omega \frac{\partial f(\omega)}{\partial \omega} \quad (33)$$

or

$$(T_1T)^{-1} = Ck_B(N_0)^2. \quad (34)$$

¹³ P. Nozières, *Le Problème à N corps* (Dunod, Paris, 1963), Chap. 4. [translation: *Theory of Interacting Fermi Systems* (W. A. Benjamin, Inc., New York, 1963)].

This result is exactly the same as the weak-coupling answer. It agrees with the experimental conclusion that the product T_1T is temperature independent.

Thus, we see that the Migdal approach is preferable to the quasiparticle approach. It is more firmly based theoretically. It leads to much simpler calculations. Its conclusions agree with experiment while the predictions of the quasiparticle approach fail badly.

ACKNOWLEDGMENTS

I would like to thank Professor John Bardeen for pointing out the existence of the discrepancy between the quasiparticle theory and experiment and also Professor C. P. Slichter for helpful discussions of the experimental situation.

APPENDIX. CALCULATION OF W_{mn}

We employ second-order time-dependent perturbation theory to calculate W_{mn} , with the interaction

$$V(t) = (8\pi/3)\gamma_e\gamma_n\mathbf{S}(\mathbf{r},t)\cdot\mathbf{I}(t), \quad (\text{A1})$$

where $\mathbf{I}(t)$ is the nuclear spin and $\mathbf{S}(\mathbf{r},t)$ is the electronic spin density at the nucleus. The result is

$$W_{mn} = \left(\frac{8\pi}{3}\gamma_e\gamma_n\right)^2 \sum_{\alpha\beta} \int dt' \langle n | I_\alpha(t) | m \rangle \langle m | I_\beta(t') | n \rangle \times \langle S_\alpha(\mathbf{r},t) S_\beta(\mathbf{r},t') \rangle. \quad (\text{A2})$$

Here the $\langle \rangle$ indicate an electronic average in the equilibrium state of the electrons alone.

We assume rotational invariance about any nuclear site in the metal. This assumption leads to

$$\langle S_\alpha(\mathbf{r},t) S_\beta(\mathbf{r},t') \rangle = \delta_{\alpha,\beta} \langle S_z(\mathbf{r},t) S_z(\mathbf{r},t') \rangle, \quad (\text{A3})$$

where S_z is expressible in terms of the usual second quantized creation and annihilation operators as

$$S_z(\mathbf{r},t) = \frac{1}{2} [\psi_\uparrow^\dagger(\mathbf{r},t)\psi_\uparrow(\mathbf{r},t) - \psi_\downarrow^\dagger(\mathbf{r},t)\psi_\downarrow(\mathbf{r},t)]. \quad (\text{A4})$$

Since

$$\langle m | I_\alpha(t') | n \rangle = e^{i(E_m - E_n)t'} \langle m | I_\alpha | n \rangle \quad (\text{A5})$$

(A2) may be written as

$$W_{mn} = \left(\frac{8\pi}{3}\gamma_e\gamma_n\right)^2 \sum_\alpha \langle n | I_\alpha | m \rangle \langle m | I_\alpha | n \rangle F(E_m - E_n) \quad (\text{A6})$$

with

$$F(E_m - E_n) = \frac{1}{4} \int dt' e^{-i(E_m - E_n)(t - t')} \times \langle [\psi_\uparrow^\dagger(\mathbf{r},t)\psi_\uparrow(\mathbf{r},t) - \psi_\downarrow^\dagger(\mathbf{r},t)\psi_\downarrow(\mathbf{r},t)] \times [\psi_\uparrow^\dagger(\mathbf{r},t')\psi_\uparrow(\mathbf{r},t') - \psi_\downarrow^\dagger(\mathbf{r},t')\psi_\downarrow(\mathbf{r},t')] \rangle. \quad (\text{A7})$$

For free electrons in the grand canonical ensemble

$$\begin{aligned} & \langle \psi_\uparrow^\dagger(1')\psi_\uparrow(1)\psi_\uparrow^\dagger(2')\psi_\uparrow(2) \rangle \\ &= \langle \psi_\uparrow^\dagger(1')\psi_\uparrow(1) \rangle \langle \psi_\uparrow^\dagger(2')\psi_\uparrow(2) \rangle \\ & \quad + \langle \psi_\uparrow^\dagger(1')\psi_\uparrow(2) \rangle \langle \psi_\uparrow(1)\psi_\uparrow^\dagger(2') \rangle, \quad (\text{A8}) \end{aligned}$$

where $1' = (\mathbf{r}',t')$, etc. The second term comes from the effect of the indistinguishability of two electrons of spin up. When particles of opposite spin are involved, this term is lacking, that is

$$\begin{aligned} & \langle \psi_\uparrow^\dagger(1')\psi_\uparrow(1)\psi_\downarrow^\dagger(2')\psi_\downarrow(2) \rangle \\ &= \langle \psi_\uparrow^\dagger(1')\psi_\uparrow(1) \rangle \langle \psi_\downarrow^\dagger(2')\psi_\downarrow(2) \rangle. \quad (\text{A9}) \end{aligned}$$

Equations (A8) and (A9) are only correct when there is no interactions between electrons. Thus, for example, the existence of a Coulomb interaction between electrons invalidate these relations. However, Migdal¹¹ has shown that the electron-phonon interaction produces only very small corrections to these relations. In particular, when indices are set equal as in (A7) the corrections to (A8) and (A9) are of order $(\omega_e/E_F) \sim 10^{-2}$. Therefore, to this order, we can employ (A8) and (A9) in evaluating (A7) as

$$F(E_m - E_n) = \frac{1}{2} \int dt' e^{-i(E_m - E_n)(t - t')} \langle \psi_\uparrow^\dagger(\mathbf{r},t)\psi_\uparrow(\mathbf{r},t') \rangle \times \langle \psi_\uparrow(\mathbf{r},t)\psi_\uparrow^\dagger(\mathbf{r},t') \rangle. \quad (\text{A10})$$

The functions $G^>(k,\omega)$ and $G^<(k,\omega)$ which we used in our previous analysis are defined for a translationally invariant system as

$$\begin{aligned} & \langle \psi_\uparrow(\mathbf{r},t)\psi_\uparrow^\dagger(\mathbf{r}',t') \rangle \\ &= \int \frac{d^3k}{(2\pi)^3} \frac{d\omega}{2\pi} G^>(k,\omega) e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}') - i\omega(t-t')} \quad (\text{A11}) \end{aligned}$$

and

$$\begin{aligned} & \langle \psi_\uparrow^\dagger(\mathbf{r}',t')\psi_\uparrow(\mathbf{r},t) \rangle \\ &= \int \frac{d^3k}{(2\pi)^3} \frac{d\omega}{2\pi} G^<(k,\omega) e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}') - i\omega(t-t')}. \quad (\text{A12}) \end{aligned}$$

Since we are neglecting all effects but those that arise from the electron-phonon interaction we can use these functions which are appropriate for the translationally invariant case. Then, (A10) becomes

$$\begin{aligned} F(E_m - E_n) &= \frac{1}{2} \int \frac{d^3k}{(2\pi)^3} \int \frac{d^3k'}{(2\pi)^3} \int \frac{d\omega}{2\pi} \\ & \quad \times \int \frac{d\omega'}{2\pi} G^<(k,\omega) G^>(k',\omega') \\ & \quad \times 2\pi\delta(\omega + E_m - \omega' - E_n), \quad (\text{A13}) \end{aligned}$$

which is Eq. (2) above.