Superconductivity in Cu and Pt by Means of Superimposed Films with Lead

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The study of normal-superconducting sandwiches provides information on the type of electron-electron interaction taking place in the normal metal. The magnitude and sign of the interaction is obtained by comparing a characteristic length which measures the depth of penetration of electron pairs in the normal metal with the effective coherence length. In order to study the electron-electron interaction in copper and platinum, superimposed films of lead-platinum and of lead-copper were deposited on glass substrates kept at 77°K. It has been shown that the effective coherence length should be calculated from the coefficient of normal electronic specific heat and the residual resistivity. The data were then plotted in such a way as to exhibit all the temperature dependence in one term, and the slope of such a plot is the depth of penetration of electron pairs in the normal metal. With the experimental accuracy presently available, the electron-electron interaction in platinum can be bracketed between -0.25 (repulsive interaction) and an attractive interaction of $+0.09$ ($T_c=2\times10^{-3}$°K). In the case of copper, the data correspond to a transition temperature of about 6 mdeg.

SUPERIMPOSED films of lead-platinum and of lead-copper were deposited on glass substrates kept at 77°K. The purpose for studying normal superconducting sandwiches is to learn what type of electron-electron interaction is taking place in the normal metal. If the interaction is attractive, there is a finite superconducting transition temperature for that metal; if repulsive, there is no transition temperature within the framework of the BCS theory, regardless of how pure the metal or how low the temperature. With the experimental accuracy presently available, the electron-electron interaction in platinum V_{Pt} can be bracketed between -0.25 (repulsive interaction) and an attractive interaction corresponding to a transition temperature of 2 mdeg. In the case of copper, the data correspond to a transition temperature of approximately 6 mdeg.

The magnitude and sign of the interaction is obtained by comparing a characteristic length[1] k^{-1} which measures the depth of penetration of electron pairs in the normal metal with the coherence length

$$\xi_n=(\hbar v_{Fn}l_n/6\pi k_B T_c)^{1/2},$$

where v_{Fn} is the velocity of Fermi surface electrons, l_n is the mean free path in the normal metal, and T_c is the transition temperature of the sandwich. If k^{-1}, the experimentally determined length, is greater than ξ_n, then the electron-electron interaction in the normal metal is attractive and the metal is a superconductor. It will be shown that in order to estimate ξ_n, the parameters v_{Fn} and l_n cannot be calculated with the free electron theory, but instead the product $v_{Fn}l_n$ should be evaluated in terms of ρ, the bulk residual resistivity, and γ, the coefficient of normal electronic specific heat. Furthermore, as ξ_n is temperature-dependent, the theory[1,2] will be rearranged so that all the temperature dependence is included in one term and k^{-1} can be compared to a temperature-independent coherence length in which T_c is replaced by T_{cs}, the transition temperature of the pure bulk superconductor.

A number of recent experiments[3–6] have described the transition temperature of superconducting normal sandwiches. Hilsch's[7] experiments on lead-copper sandwiches are particularly interesting as the films were deposited at 10°K and kept below 100°K until measured. This technique minimizes such spurious effects as diffusion.[5] Furthermore, Hilsch measured the residual resistivities of the films, which are necessary in order to interpret the experiments in terms of existing theories.[1,2] When the normal metal, copper, is kept at a constant thickness, the transition temperature of the sandwich decreases from 7.2°K as the lead film is decreased in thickness from 1000 to 100 Å (if the lead film was deposited first, the drop in transition temperature was less than when the copper film was deposited first). If, on the other hand, the lead films are kept at a constant thickness, the transition temperature decreases exponentially from 7.2°K to an asymptotic value Θ as the normal film thickness is increased. The magnitude of Θ depends on the thickness of the superconducting film. Hilsch first pointed out on purely empirical grounds the following two relations:

$$7.2-T_c=(7.2-\Theta)(1-e^{-d_{\mathrm{Cu}}/a}), \quad (1)$$

$$a^2\rho=1.7\times10^{-17}\Omega\text{-cm}^3, \quad (2)$$

where T_c is the transition temperature of the sandwich, d_{Cu} the thickness of the copper film, and the constant a

[1] P. G. De Gennes and E. Guyon, Phys. Letters **3**, 168 (1963). P. G. De Gennes, Rev. Mod. Phys. **36**, 225 (1964).
[2] N. R. Werthamer, Phys. Rev. **132**, 2440 (1963).
[3] H. Meissner, Phys. Rev. **117**, 672 (1960); IBM J. Res. Develop. **6**, 71 (1962).
[4] P. H. Smith, S. Shapiro, J. L. Miles, and J. Nicol, Phys. Rev. Letters **6**, 686 (1961).
[5] A. C. Rose-Innes and B. Serin, Phys. Rev. Letters **7**, 278 (1961).
[6] W. A. Simmons and D. H. Douglass, Jr., Phys. Rev. Letters **9**, 153 (1962).
[7] P. Hilsch, Z. Physik **167**, 511 (1962).

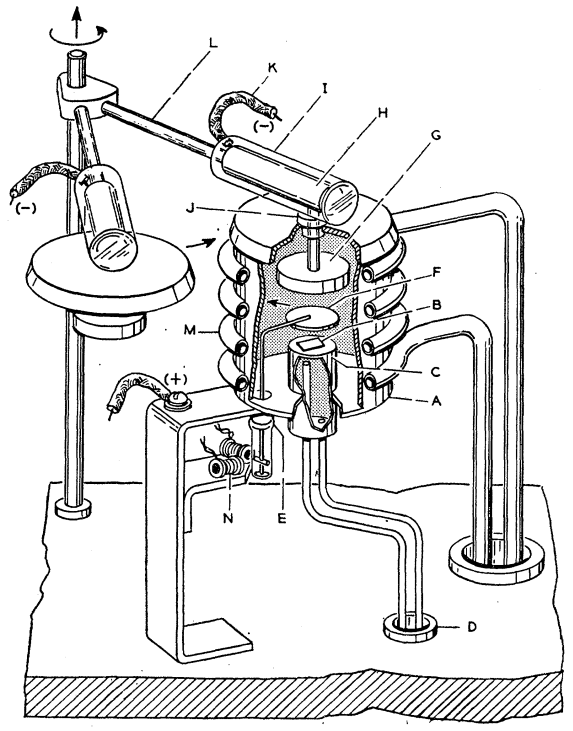

FIG. 1. Getter-sputtering apparatus used for sandwich deposition. A: Anode can. B: Substrate. C: Liquid-nitrogen cold table. D: Liquid-nitrogen feed-through. E: Covar-glass seal. F: Tantalum shield. G: Electrode. H: Electrode holder. I: Quartz shield. J: Quartz bushing. K: Shielded negative lead. L: Quartz supported rod. M: Liquid-nitrogen cooling coil. N: Electromagnet.

is correlated with the bulk residual resistivity of copper by relation (2).

In the experiments reported here, the films were deposited at liquid-nitrogen temperature by the getter-sputtering technique.[8] The apparatus used for deposition is shown in Fig. 1. The sandwiches were always kept below 150°K until measured. The results on Pb-Cu sandwiches are shown in Fig. 2. The data can be fitted approximately by relation (1) with $a=130$ Å and $\Theta=1.4$°K. As in these experiments, $\rho=10\times10^{-6}\,\Omega$-cm, $a^2\rho$ has the same constant value as observed by Hilsch in relation (2).

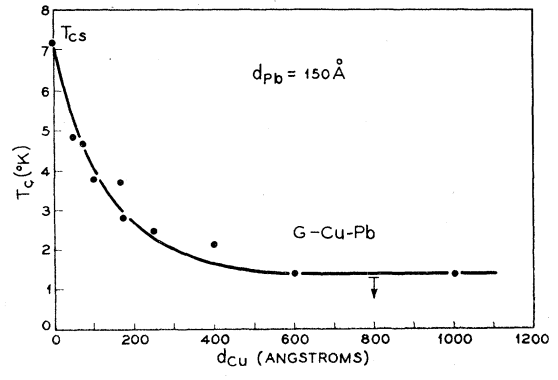

FIG. 2. Transition temperature of Pb-Cu sandwiches for a constant lead film thickness of 150 Å.

The data on the Pb-Pt system are shown in Figs. 3 and 4. In Fig. 3, the normal metal Pt is kept at a constant thickness of 1000 Å, and again one notices a reduction of the drop in transition temperature when the Pb is deposited first. In Fig. 4, the superconducting metal Pb is kept at a constant thickness of 300 Å, and the data can be fitted approximately by relation (1). Although the Θ values are quite different, depending on whether the Pb is deposited first or last, the exponential constant a is 37 Å when the Pb is deposited first, and 45 Å when deposited last; as the accuracy in determining film thickness is only $\pm10\%$, the difference between these two numbers may not be meaningful. There are two conceivable ways to explain the different reductions in T_c depending on the order of deposition

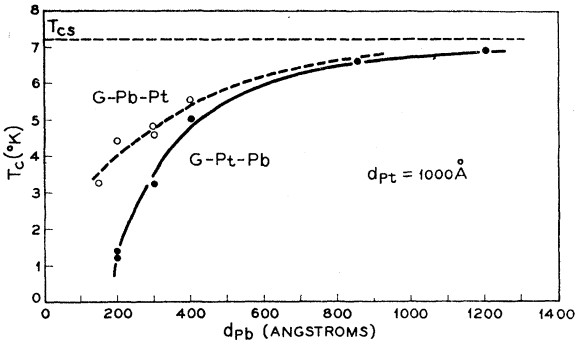

FIG. 3. Transition temperature of glass Pt-Pb and of glass Pb-Pt sandwiches for a constant platinum film thickness of 1000 Å.

of the metals. First, one may argue that the grain size of the superconducting lead will be different depending on whether the lead is deposited on glass or on either platinum or copper. This difference in grain size will, in turn, produce a difference in mean free path and consequently, a different effective coherence length.[9] However, as the same should be true of the normal metals Cu and Pt, this should be reflected in a different ρ, and consequently, in a different constant a, which is not the case. On the other hand, even in the good vacuum used by Hilsch and in the present experiments, it is impossible to prevent the formation of a few monolayers of oxide on the film first deposited. As lead is more oxidizable than either Cu or Pt, the films comprising the sandwich will be further apart when lead is deposited first. As De Gennes[1] first pointed out, such an effect will reduce the drop in T_c without changing the constant a.

[8] H. C. Theuerer and J. J. Hauser, J. Appl. Phys. 35, 554 (1964).

[9] J. J. Hauser and H. C. Theuerer, Phys. Rev. 134, A198 (1964).

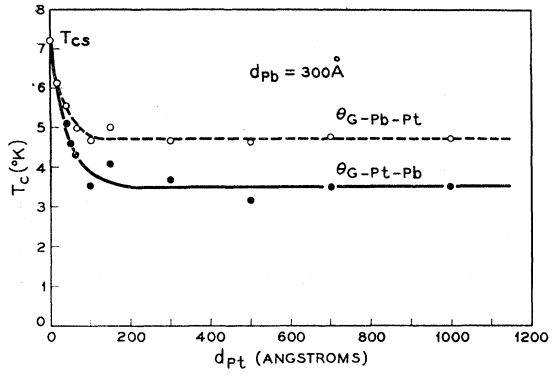

FIG. 4. Transition temperature of glass Pb-Pt and of glass Pt-Pb sandwiches for a constant lead film thickness of 300 Å.

De Gennes[1] has developed a theory which explains Hilsch's experiments. In the "one-frequency" limit, he used to solve the Gor'kov equations, valid when d_n and d_s are, respectively, larger than ξ_n and ξ_s, he showed that

$$T_c=\Theta+Ce^{-2kd_n}, \tag{3}$$

where C is a constant. The decay constant $2k$ is inversely proportional to $(l_{\mathrm{Cu}})^{1/2}$ in agreement with Hilsch's relation (2) since

$$k^{-1}=2a. \tag{4}$$

In order to calculate the interaction in the normal metal, one must use the following equation[1]:

$$k^2=(1/\xi^2)(1-2NV/1-CNV)\,, \tag{5}$$

where

$$C=\ln(1.14\Theta_D/T_c)-2.$$

The value of k is determined experimentally via relation (4); Θ_D is the Debye temperature of the normal metal, N is the density of states, and ξ, is the effective coherence length which is defined as

$$\xi=(\hbar v_F l/6k_B T_c)^{1/2}. \tag{6}$$

As this theory is only valid for films that are thick compared to the coherence length, the depression in the transition temperature should be very small, and therefore De Gennes replaced T_c by 7°K in relation (6). Using a free-electron value for v_F and l_{Cu}, $\xi_{\mathrm{Cu}}=190$ Å. As Hilsch found that $a=100$ Å and $k^{-1}=200$ Å, using relation (5), De Gennes concluded that $(NV)_{\mathrm{Cu}}\simeq+0.05$, which corresponds to a transition temperature of a few mdeg.

If one applies the same reasoning to the Pb-Pt system, i.e., use $T_c=7$°K and calculate v_F and l from a free-electron theory with $\rho_{\mathrm{Pt}}=30\times10^{-6}$ Ω-cm, then $\xi_{\mathrm{Pt}}=180$ Å. Furthermore, our measurements give $a\simeq40$ Å or $k^{-1}=80$ Å [from relation (4)]. But this is impossible because, as can be seen from relation (5), the minimum value of k^{-1} which corresponds to $(NV)=-\infty$ is 120 Å. This discrepancy will now be corrected in two steps. First of all, although it may be correct to use free-electron theory for copper, it is certainly not justifiable for platinum. Instead, we us the following relations established by Pippard[10]:

$$\sigma=e^2S\langle l\rangle/12\pi^3\hbar,\quad \gamma=k_B^2S/12\pi\hbar\langle v_F\rangle\,, \tag{7}$$

where S is the Fermi surface area and the brackets mean averaging over the Fermi surface. Combining relations (7), one obtains

$$v_F l=(\pi k_B/e)^2(\sigma/\gamma)\,, \tag{8}$$

which permits one to estimate $v_F l$ from the experimentally measured quantities σ and γ. The substitution of relation (8) in Eq. (6) yields a result which actually is general for any Fermi surface.

In the case of platinum, using $\rho=30\times10^{-6}$ Ω-cm and $\gamma=6.41\times10^{-3}$ J/°K² mole,[11] one finds for $T_c=7.2$°K, $\xi_{\mathrm{Pt}}=44$ Å. If one now compares this value of ξ with $k^{-1}=80$ Å, relation (5) would yield an incredibly high transition temperature for platinum. This discrepancy is due to the fact that De Gennes' theory[1] is only valid for films much thicker than the coherence length, where the reduction in transition temperature is small and T_c is close to $T_{cs}=7.2$°K. On the other hand, in the experiments described in Fig. 4 as well as those of Hilsch, the drop in transition temperature is large and such a theory cannot be applied.

Werthamer[2] has established a theory which is not limited by the same restrictions as that of De Gennes. By merging the two theories to remove the weak points of each, the following two relations in the superconductor and the normal metal have been derived.

$$\ln(T_{cs}/T_c)=\chi(\xi_s^2k_s^2)\ln(T_c/T_{cn})=-\chi(-\xi_n^2k_n^2)\,, \tag{9}$$

where

$$\chi(Z)\equiv\psi(\tfrac{1}{2}+\tfrac{1}{2}Z)-\psi(\tfrac{1}{2})$$

and ψ is the digamma function. In addition, we have the boundary condition

$$[N\xi^2k\tan kd]_s=[N\xi^2k\tanh kd]_n. \tag{10}$$

Although Eqs. (9) and (10) completely define the problem, we find it convenient for simplifying the analysis to replace $\chi(Z)$ by $\ln[1+(\pi^2/4)Z]$ for $Z\geq0$. The first of relations (9) then becomes

$$k_s=(2/\pi\xi_{ss})(1-t)^{1/2}, \tag{11}$$

where ξ_{ss} is the coherence length (6) of the superconductor at $T_c=T_{cs}$, and t is the reduced temperature. Taking the limit in Eqs. (10) and (11) of $k_nd_n\to\infty$ so that $t\to\theta\equiv\Theta/T_{cs}$, we find

$$N_s\xi_{ss}(2/\pi)(\theta^{-1}-1)^{1/2}\tan k_s(\theta)d_s=N_n\xi_{ns}\xi_n(\theta)k_n(\theta)\,. \tag{12}$$

[10] A. B. Pippard, Rept. Progr. Phys. **23**, 176 (1960).
[11] D. W. Budworth, F. E. Hoare, and J. Preston, Proc. Roy. Soc. (London) **A257**, 250 (1961).

Substituting Eqs. (11) and (12) into (10) and solving for d_n leads to

$$d_n=\frac{1}{k_n}\tanh^{-1}\left\{\frac{(t^{-1}-1)^{1/2}\tan k_s(t)d_s}{(\theta^{-1}-1)^{1/2}\tan k_s(\theta)d_s}\left(\frac{\xi_n(\theta)k_n(\theta)}{\xi_n(t)k_n(t)}\right)\right\}. \quad (13)$$

If $T_{cn}\simeq 0$, the last term in the parenthesis in relation (13) is very close to unity. If one further assumes that θ is sufficiently low so that $k_s d_s \ll 1$, one can replace $\tan x$ by x, and one finally obtains after some algebraic manipulations

$$d_n=k^{-1}\left[\frac{1}{2t^{1/2}}\ln\left(\frac{1+[(1-t)/(1-\theta)](\theta/t)^{1/2}}{1-[(1-t)/(1-\theta)](\theta/t)^{1/2}}\right)\right]. \quad (14)$$

The interesting feature of relation (14) is that all the temperature dependence has been collected into one term. If one plots the thickness of the normal film versus the temperature-dependent term in the bracket, one should get a straight line with slope k^{-1}. Furthermore, expression (14) is valid precisely in the limit of thin films where the reduction in transition temperature is large, which is the case where the greatest experimental accuracy can be expected.

The data shown in Fig. 4 for the Pb-Pt system have now been plotted according to Eq. (14) in Fig. 5. One does indeed observe the straight-line plot expected theoretically, and allowing for a 10% error in estimating the film thickness, k^{-1} can be bracketed between 37 and 49 Å. Using $\xi_{ns}=44$ Å [where $\xi_{ns}=\xi_n(T_c=T_{cs})$] in relation (5), the lower limit of k^{-1} corresponds to a repulsive interaction $NV=-0.25$, while the upper limit gives an attractive interaction $NV=+0.085$ or $T_{c_{Pt}}=2\times10^{-3}$°K. This prediction is extremely sensitive to small errors in determining the film thickness. The theory demands data of greater and greater accuracy to determine with precision normal-metal transition temperatures approaching 0°K.

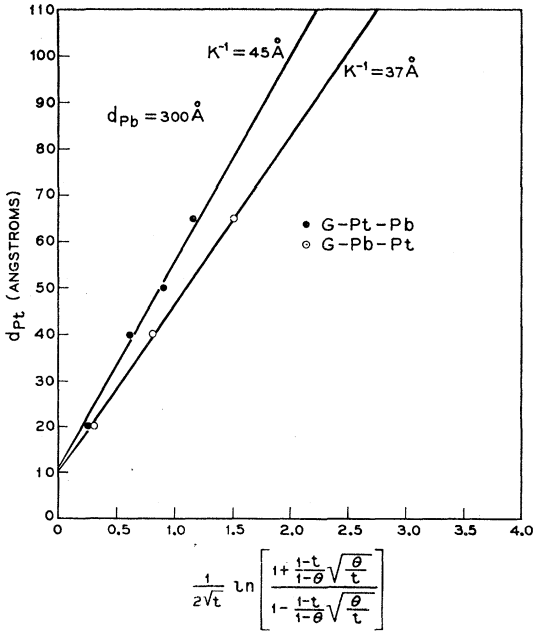

FIG. 5. Plot of platinum film thickness versus temperature reduced according to relation (14) for a constant lead film thickness of 300 Å.

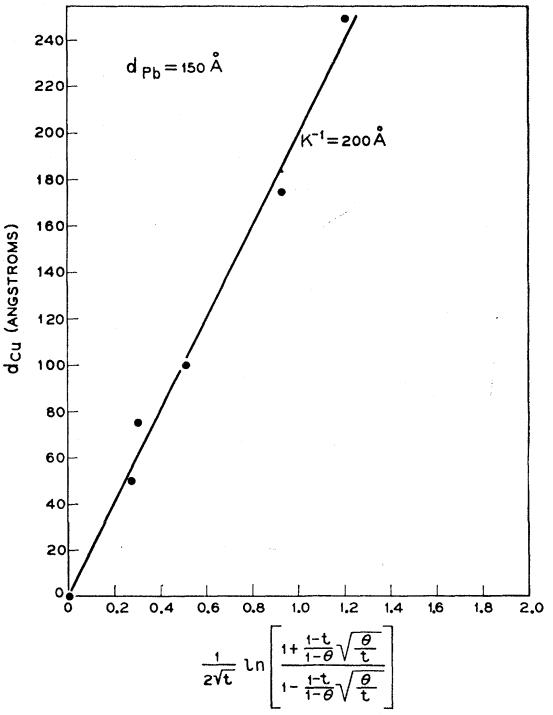

FIG. 6. Plot of copper film thickness versus temperature reduced according to relation (14) for a constant lead film thickness of 150 Å.

It is obvious from relation (14) that $t=1$ or $T_c=T_{cs}$ must correspond to $d_n=0$. On the other hand, the data of Fig. 5 extrapolate to $d_n=10$ Å as $t\rightarrow 1$. This can be explained if one assumes that the film surface roughness is of the order of 10 Å; and consequently, the measured transition temperature of the sandwich corresponds to the thinnest portions of the platinum film. To check this assumption, a platinum film of average thickness 10 Å was deposited, and this film was not electrically continuous.

Turning to the case of copper, the data shown in Fig. 2 can be replotted according to Eq. (14), and one obtains the straight-line plot shown in Fig. 6 with a slope $k^{-1}=200$ Å. In these experiments, $\rho=10\times10^{-6}$ Ω-cm, and $\gamma_{Cu}=2.1\times10^{-4}$ cal/°K² mole[12] so that, using relations (6) and (8), one finds $\xi_{Cu}=180$ Å. Substituting these values into Eq. (5) one is led to predict a transition temperature of 6×10^{-3}°K for copper. The accu-

[12] C. A. Shiffman, G.E. Report, 1952 (unpublished).

racy of this number is of course subject to the same restrictions as discussed before in the case of platinum.

In conclusion, it has been shown that the effective coherence length of the normal metal should be calculated from the coefficient of normal electronic specific heat and the residual resistivity. If the data are then plotted in such a way as to exhibit all the temperature dependence in one term, one gets a linear plot of which the slope (k^{-1}) is very close to the calculated coherence length. Since the electron-electron interaction in both Pt and Cu was found to be very close to zero, any more accuracy prediction for these metals will have to await much more precise film thickness control or measurements at even lower laboratory temperatures.

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Error Estimates in the Variational Many-Boson Calculation

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A simple test, recently suggested by Armstrong, is used to estimate the quality of the variational wave function first used by Aviles and Iwamoto in treating the ground state of the hard-sphere many-boson system. In this special case, Armstrong's method can be simplified by using a result obtained by Lieb in his recent work on the ground-state energy of the Bose gas. The wave function was previously used by the author to compute a first-order correction to the energy, due to a weak additional interaction outside the hard sphere. The errors in this computation are in good agreement with the estimates obtained by Armstrong's method.

A SIMPLE test, to be used in conjunction with a standard Rayleigh-Ritz variational method, to give some estimate of the accuracy of the trial function has recently been suggested by Armstrong.[1] He integrates the Schrödinger equation over all space, and obtains an expression for the energy

$$E_{NV}=\int dv H\psi \Big/ \int dv\psi, \tag{1}$$

provided the integral in the denominator is nonvanishing.[2] This is compared with the corresponding variational expression using the same trial function

$$E_V=\int dv\psi^* H\psi \Big/ \int dv|\psi|^2, \tag{2}$$

and the difference E_V-E_{NV} between the two is a rough indicator of the quality of ψ.[3] The original applications of the method[1] were to standard one- and two-particle systems, including the ground state of helium.

It is the purpose of the present note to apply this procedure to a many-body system, previously extensively considered by several authors[4–7] from a variational point of view. This system is the boson hard-sphere gas with[7] or without[4–6] an additional weak attraction or repulsion.

The variational method is very clearly described by Aviles.[4] A product trial function

$$\psi(\mathbf{r}_1\cdots\mathbf{r}_N)=\prod_{i<j}^{N} f(\mathbf{r}_i-\mathbf{r}_j) \tag{3}$$

is used to approximate the ground-state solution of the Hamiltonian

$$H=-(\hbar^2/2m)\sum_{i=1}^{N}\nabla_i^2+\sum_{i<j}^{N} V(\mathbf{r}_i-\mathbf{r}_j)\,. \tag{4}$$

The hard-sphere boundary condition requires that

$$f(\mathbf{r})=0, \quad \text{for} \quad r\leq r_0, \tag{5}$$

while $V(\mathbf{r})$ is the additional weak interaction.[7] The

[1] B. H. Armstrong, Bull. Am. Phys. Soc. **9**, 401 (1964), and private communication.

[2] If the denominator vanishes, it may be possible to rewrite Eq. (1). For example, if ψ has angular momentum different from zero, the Schrödinger equation in partial waves can be used to reformulate Eq. (1) in unambiguous form.

[3] Certain special choices of ψ may accidentally give $E_V=E_{NV}$ without, in fact, corresponding to exact solutions. A notable case, observed by the author and Armstrong independently, is the trial function $\exp[-\alpha(r_1+r_2)]$ often used for the helium atom [E. Merzbacher, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1961), pp. 430–436]. These special cases can be easily shown not to satisfy the eigenvalue equation.

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