

The case of CdF_2 is obviously different. Little thermoluminescence is observed. In general, this crystal exhibits an entirely different behavior than CaF_2 and its isomorphs. Trivalent rare earths in CdF_2 cannot be reduced to the divalent state by chemical baking; instead, the crystal displays the properties of a semiconductor when doped with several of the rare earths.²⁹

²⁹ P. F. Weller, *Inorg. Chem.* **4**, 1545 (1965).

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Effect of Paramagnetic Impurity on the Long Lifetime of Positron in Liquid Ammonia

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We have computed the paramagnetic quenching effect of lithium and sodium in liquid ammonia on the long-lifetime component of positron annihilation. The triplet-to-singlet conversion cross sections, calculated in the Born approximation, turn out to be $5.9 \times 10^{-14} \text{ cm}^2$ for Li and $7.2 \times 10^{-14} \text{ cm}^2$ for Na for thermalized positronium. Reasonable agreement with the meagre existing experimental data is obtained.

I. INTRODUCTION

IT has been known for quite some time that the two-quantum annihilation spectra of positrons in many liquids and gases show a long-lived τ_2 component and that this lifetime is affected appreciably by the presence of paramagnetic impurities.¹ Any process whereby the two-photon annihilation replaces the longer-lived three-photon annihilation and contributes to the τ_2 component is called quenching. Heynman, Osman, Veit, and Williams² discuss various types of processes involved—unpaired-electron exchange, angular-momentum reorientation, chemical-compound formation, pickoff, and spin reversal. The explanation of paramagnetic quenching is as follows: Orthopositronium (triplet) is formed first and is subsequently converted by electron-exchange collisions in the medium to the parapositronium (singlet), which then decays promptly. The paramagnetic impurity introduced into the medium provides extra electrons that can be exchanged easily with the electron in positronium. Since the latter does not have magnetic moment in either of the two states involved, magnetic forces can be neglected. It has been emphasized by Ferrell³ that the naive interpretation of the triplet to singlet conversion as a “spin-flip” process of the paramagnetic impurity is not correct. Rather one must consider the

electron exchange arising essentially from the anti-symmetrization requirements on the wave function of a many-electron problem.

A direct first-principle calculation of τ_2 embracing all aspects of the quenching would be difficult. However, the modification of τ_2 by a small concentration of paramagnetic impurities would be easier to compute, particularly when the scatterers are isolated. A theoretical calculation of the triplet to singlet conversion in collisions of orthopositronium with atomic hydrogen was given by Massey and Mohr,⁴ using the Born approximation. A more detailed calculation for the same system was given by Fraser⁵ who found that the Born approximation result was too high, as one would have expected, and that the cross section fell off rapidly with energy on the scale of electron volts. On the experimental side, positron annihilation in atomic hydrogen has not been studied so far. Other quenching agents such as oxygen and nitric oxide, or diphenylpicrylhydrazyl (DPPH) in liquid benzene require a calculation of scattering from complex molecules. Obviously, one would like to have a system sufficiently simple and hydrogenlike where calculations can be attempted and meaningfully compared with experiments; such a situation prevails in the study of positron annihilation in solutions of lithium and sodium in ammonia.⁶

¹ See for earlier work the review article by M. Deutsch and S. Berko, in *Alpha-, Beta-, and Gamma-Ray Spectroscopy*, edited by K. Sieghahn (North-Holland Publishing Company, Amsterdam, 1965), Vol. 2, p. 1583.

² F. F. Heynman, P. Osman, J. J. Veit, and W. F. Williams, *Proc. Phys. Soc. (London)* **78**, 1038 (1961).

³ R. Ferrell, *Phys. Rev.* **110**, 1355 (1958).

⁴ H. S. W. Massey and C. B. O. Mohr, *Proc. Phys. Soc. (London)* **A67**, 695 (1954).

⁵ P. A. Fraser, *Proc. Phys. Soc. (London)* **79**, 721 (1961).

⁶ See T. P. Das [in *Advances in Chemical Physics*, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1962), Vol. 4, p. 303] for an account of their properties.

It has been reported that sodium dissolved to saturation in ammonia quenches the long lifetime completely.⁷ In a recent work Varlashkin and Stewart⁸ report a series of angular-correlation studies of lithium-ammonia, which reveal at low concentration the existence of a bound state. They do not make any lifetime measurements, with which we are concerned. Some preliminary measurements of the lifetime were reported by Millet *et al.*,⁹ and as far as we can judge, the theoretical calculations give the right order of magnitude for lifetime.

Although the alkali atoms are hydrogenlike, the calculation of the quenching is rather involved. We assume that at very low concentrations the alkali atoms in ammonia retain their atomic character and the chemical effect of the solution is negligible. The entire purpose of the ammonia solution (apart from its own quenching mechanism to generate a τ_2 component) is to provide a slowing-down medium of the positronium, and we consider the triplet positronium to be completely thermalized. The problem is then to compute the scattering of the low-energy positronium on the alkali atoms. The conversion cross section is calculated in the Born approximation at zero momentum transfer—this latter for convenience of evaluation—and we use the limiting value over the thermal energy region. At very low concentrations when individual scatterers act independently, modification of τ_2 is linear in the concentration of alkali atoms. Such dilution is necessary for positronium formation. At the opposite extreme of high densities when the metallic character of sodium begins to appear, this is not possible¹⁰; even the concept of bound state loses its significance.¹¹

In treating the alkali atoms as hydrogen like we are ascribing the entire quenching effect essentially to the outermost electron. This picture emerges from our detailed numerical calculation with lithium. The effect of the inner electrons is certainly small. But as our calculation is based on the Born approximation and there are some rearrangement effects, the result cannot be completely conclusive.

We use the formulation of scattering theory of Goldberger and Watson (GW),¹² and generalize the Massey-Mohr calculation to compute the conversion cross section in ammonia. Section III presents some results which show that the contribution of the outer-

most electron, though clearly dominant, is somewhat sensitive to the details of the outer part of the wave function.

II. LITHIUM AS QUENCHING AGENT IN NH₃

If τ_2 denotes the long lifetime of pure ammonia solution, the number N of quenched decays in the presence of alkali atoms will be given by

$$dN/dt = -\tau_2^{-1}N - n\sigma vN. \quad (2.1)$$

Here n is the number of alkali atoms per cc, σ is the conversion cross section, and v is the velocity of the positronium which can be obtained from the fact that it is thermalized in the medium. The contribution of the alkali atoms is linear in their concentration. This implies that each scattering center acts independently, and no coherence between alkali atoms is present. One expects such a situation to be true at very dilute solution. At high concentration this requires modification, and coherent scatterings may have to be included.

Let us proceed with the calculation of the conversion cross section in the scattering of orthopositronium on lithium atoms. The problem is a many-electron problem, and a completely satisfactory solution is out of the question. However, treating electronic correlations in Li approximately, we can write down the entire wave function of the Li atom as a Slater determinant. Then using the Born approximation, we can write down the entire scattering amplitude involving all the four electrons, three from Li and one from positronium. There is no direct scattering amplitude connecting the incident channel of triplet positronium to the outgoing channel with singlet positronium. The nonvanishing terms are of two types. The dominant terms can be interpreted to be an exchange of the electron in the positronium with the outermost 2s electron. The interaction potential has terms that look like the hydrogenic terms⁴ and also some terms that come from the screening of the nuclear charge by the occupied 1s orbital. These additional terms are exponentially damped, and we show that they are negligible. The second kind of terms should be called rearrangement terms. They are numerically found to be small. As the Born approximation is known to be poor for rearrangement collisions, we cannot claim to have proved that all rearrangement terms are small.

Assuming the nucleus to be fixed, we can write down the Hamiltonian for the entire system:

$$H = \frac{\mathbf{p}^2}{2m} + \sum_{i=1}^4 \frac{\mathbf{p}_i^2}{2m} + \frac{3e^2}{r} - \sum_{i=1}^4 \frac{3e^2}{r_i} - \sum_{i=1}^4 \frac{e^2}{|\mathbf{r} - \mathbf{r}_i|} + \sum_{i < j}^{1,4} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (2.2)$$

⁷ B. G. Hogg, T. H. Sutherland, D. A. L. Paul, and J. W. Hodgkins, *J. Chem. Phys.* **25**, 1082 (1956).

⁸ P. G. Varlashkin and A. T. Stewart, *Phys. Rev.* **148**, 459 (1966).

⁹ W. E. Millet, L. H. Dieterman, and J. C. Thomson, in *Positron Annihilation Conference*, edited by A. T. Stewart and L. O. Roeiligg (Academic Press Inc., New York, 1967).

¹⁰ A. Held and S. Kahana, *Can. J. Phys.* **42**, 1908 (1964); H. Kanazawa, Y. H. Ohtsuki, and S. Yanagawa, *Phys. Rev.* **138**, A1155 (1965); C. K. Majumdar, Ph.D. thesis, University of California, La Jolla, California (unpublished).

¹¹ W. Kohn and C. Majumdar, *Phys. Rev.* **138**, A1617 (1965).

¹² M. L. Goldberger and K. M. Watson, *Collision Theory* (John Wiley & Sons, Inc., New York, 1964) Chap. 4.

The subscripts refer to the four electrons involved. Divide H in the incident channel into $K_c + V$ with

$$K_c = \left[\sum_{i=1}^3 \left(\frac{\mathbf{p}_i^2}{2m} - \frac{3e^2}{r_i} \right) + \sum_{M \substack{1,3 \\ i < j}} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right] + \frac{\mathbf{p}^2}{2m} + \frac{\mathbf{p}_4^2}{2m} - \frac{e^2}{|\mathbf{r} - \mathbf{r}_4|}; \quad (2.3)$$

$$V = 3e^2(r^{-1} - r_4^{-1}) + e^2 \sum_{i=1}^3 (|\mathbf{r}_4 - \mathbf{r}_i|^{-1} - |\mathbf{r} - \mathbf{r}_i|^{-1}). \quad (2.4)$$

This decomposition corresponds to electron 4 being in the positronium. The terms in the brackets in (2.3) constitute the lithium atom; the rest form the positronium. V is obviously symmetric in $\mathbf{r}_1, \mathbf{r}_2$, and \mathbf{r}_3 . Using an independent-particle model for Li, the incident-channel wave function can be written as

$$\Psi_a = \frac{1}{\sqrt{3!}} \begin{vmatrix} \phi_{2s}(\mathbf{r}_1)\chi_s(1) & \phi_{1s}(\mathbf{r}_1)\alpha(1) & \phi_{1s}(\mathbf{r}_1)\beta(1) \\ \phi_{2s}(\mathbf{r}_2)\chi_s(2) & \phi_{1s}(\mathbf{r}_2)\alpha(2) & \phi_{1s}(\mathbf{r}_2)\beta(2) \\ \phi_{2s}(\mathbf{r}_3)\chi_s(3) & \phi_{1s}(\mathbf{r}_3)\alpha(3) & \phi_{1s}(\mathbf{r}_3)\beta(3) \end{vmatrix} \frac{\exp\{i\mathbf{k} \cdot (\mathbf{r} + \mathbf{r}_4)/2\}}{(2\pi)^{3/2}} \tilde{\phi}_{1s}(|\mathbf{r} - \mathbf{r}_4|) \begin{Bmatrix} \alpha \alpha(4) \\ (1/\sqrt{2})[\alpha\beta(4) + \beta\alpha(4)] \\ \beta \beta(4) \end{Bmatrix}. \quad (2.5)$$

ϕ_{1s} and ϕ_{2s} are the Li atom orbitals. The orbitals available from the work of Wilson¹³ will be used; apart from that no correlation effects are included. α and β are the up and down spin functions, respectively, with regard to some fixed quantization axis. χ_s is the spin function of the $2s$ electron; we shall average over the initial spin states $s = \pm \frac{1}{2}$. We must antisymmetrize the fourth electron with the other three. If P_{ij} denotes the operator that exchanges the particles i and j , the completely antisymmetric wave function is¹²

$$\alpha[\frac{1}{2}\Psi_a] = \frac{1}{2}(\Psi_a - \sum_{i=1}^3 P_{4i}\Psi_a). \quad (2.6)$$

The outgoing-channel wave function is, similarly,

$$\Psi_b = \frac{1}{\sqrt{3!}} \begin{vmatrix} \phi_{2s}(\mathbf{r}_1)\chi_{s'}(1) & \phi_{1s}(\mathbf{r}_1)\alpha(1) & \phi_{1s}(\mathbf{r}_1)\beta(1) \\ \phi_{2s}(\mathbf{r}_2)\chi_{s'}(2) & \phi_{1s}(\mathbf{r}_2)\alpha(2) & \phi_{1s}(\mathbf{r}_2)\beta(2) \\ \phi_{2s}(\mathbf{r}_3)\chi_{s'}(3) & \phi_{1s}(\mathbf{r}_3)\alpha(3) & \phi_{1s}(\mathbf{r}_3)\beta(3) \end{vmatrix} \frac{\exp\{i\mathbf{k} \cdot (\mathbf{r} + \mathbf{r}_4)/2\}}{(2\pi)^{3/2}} \tilde{\phi}_{1s}(|\mathbf{r} - \mathbf{r}_4|) (1/\sqrt{2})[\alpha\beta(4) - \beta\alpha(4)]. \quad (2.7)$$

After antisymmetrization, we get

$$\alpha[\Psi_b] = \frac{1}{2}(\Psi_b - \sum_{i=1}^3 P_{4i}\Psi_b). \quad (2.8)$$

In the Born approximation, the total matrix element for scattering is¹²

$$\langle \alpha[\Psi_b] | V | \alpha[\Psi_a] \rangle = \langle \Psi_b | V | \Psi_a \rangle - \sum_{i=1}^3 \langle P_{4i}\Psi_b | V | \Psi_a \rangle. \quad (2.9)$$

Since the interaction is spin-independent it is convenient to carry out the spinology first and select the nonvanishing terms. It is immediately clear that the direct term is zero.

$$\langle \Psi_b | V | \Psi_a \rangle = 0. \quad (2.10)$$

All the remaining exchange terms give equal contribution

$$\langle P_{41}\Psi_b | V | \Psi_a \rangle = \langle P_{42}\Psi_b | V | \Psi_a \rangle = \langle P_{43}\Psi_b | V | \Psi_a \rangle = \frac{1}{3}T_{\text{ex}}. \quad (2.11)$$

Considering $\langle P_{41}\Psi_b | V | \Psi_a \rangle$ we obtain

$$\langle P_{41}\Psi_b | V | \Psi_a \rangle = \frac{1}{(2\pi)^3} \frac{2J}{3!} \times [(1/\sqrt{2})\delta_{s'\uparrow}\delta_{s\downarrow}; \frac{1}{2}(\delta_{s\downarrow}\delta_{s'\downarrow} - \delta_{s'\uparrow}\delta_{s\uparrow}); - (1/\sqrt{2})\delta_{s'\uparrow}\delta_{s\uparrow}]. \quad (2.12)$$

The expression for T_{ex} is the same without the factor $\frac{1}{3}$. We shall write down the integral J below. The second line in (2.12) shows explicitly the presence of a contribution where a naive "spin-flip" of the atomic electron does not occur—a point first emphasized by Ferrell.³ We get after averaging over the initial spin states and summing over final ones,

$$\sum_{s'} \frac{1}{2} \sum_s \frac{1}{2} \sum_{M=-1}^1 |T_{\text{ex}}|^2 = [1/(2\pi)^6] |J|^2 \frac{1}{4}. \quad (2.13)$$

¹³ E. B. Wilson, J. Chem. Phys. 1, 210 (1933).

Let us examine J . After some simple algebra, we get

$$\begin{aligned}
 J = & \int \exp\{-i\mathbf{k}' \cdot (\mathbf{r} + \mathbf{r}_1)/2\} \exp\{i\mathbf{k} \cdot (\mathbf{r} + \mathbf{r}_4)/2\} \tilde{\phi}_{1S}(|\mathbf{r} - \mathbf{r}_1|) \tilde{\phi}_{1S}(|\mathbf{r} - \mathbf{r}_4|) V(\mathbf{r}, \mathbf{r}_4; \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\
 & \times [\varphi_{2S}(\mathbf{r}_4) \varphi_{2S}(\mathbf{r}_1) \varphi_{1S}^2(\mathbf{r}_2) \varphi_{1S}^2(\mathbf{r}_3) - \varphi_{2S}(\mathbf{r}_4) \varphi_{1S}(\mathbf{r}_1) \varphi_{1S}(\mathbf{r}_2) \varphi_{2S}(\mathbf{r}_2) \varphi_{1S}^2(\mathbf{r}_3) + \varphi_{1S}(\mathbf{r}_4) \varphi_{1S}(\mathbf{r}_1) \varphi_{2S}(\mathbf{r}_2) \\
 & \times \varphi_{1S}(\mathbf{r}_2) \varphi_{1S}(\mathbf{r}_3) \varphi_{2S}(\mathbf{r}_3) - \varphi_{1S}(\mathbf{r}_4) \varphi_{2S}(\mathbf{r}_1) \varphi_{2S}(\mathbf{r}_2) \varphi_{1S}(\mathbf{r}_2) \varphi_{1S}^2(\mathbf{r}_3)] d\mathbf{r} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4. \quad (2.14)
 \end{aligned}$$

At this point we make use of the assumption that k and k' are both very small and lie in the thermal region, so that $ka_0, k'a_0 \ll 1$, where a_0 is the Bohr radius. In other words, a good approximation to J for our purpose may be obtained by calculating it for $k = k' = 0$. One must remember that it is not known whether the positronium is thermalized; however, in a solid or liquid, this seems more likely than in a gas. A rapid change of quenching with temperature, if observed, may mean some difficulties with this assumption; so far, this has not been reported. The third term vanishes because of the orthogonality in ϕ_{1S} and ϕ_{2S} ; for it involves a change of state of both particles 2 and 3, while V allows only one such change. The second and fourth terms will be considered below.

The first term gives the main contribution. Writing it out in full,

$$\begin{aligned}
 J_1 = & \int d\mathbf{r} d\mathbf{r}_1 d\mathbf{r}_4 \tilde{\phi}_{1S}(|\mathbf{r} - \mathbf{r}_1|) \tilde{\phi}_{1S}(|\mathbf{r} - \mathbf{r}_4|) \varphi_{2S}(\mathbf{r}_4) \varphi_{2S}(\mathbf{r}_1) [3e^2(r^{-1} - r_4^{-1}) + e^2(|\mathbf{r}_4 - \mathbf{r}_1|^{-1} - |\mathbf{r} - \mathbf{r}_1|^{-1})] \\
 & + \int d\mathbf{r} d\mathbf{r}_1 d\mathbf{r}_4 \tilde{\phi}_{1S}(|\mathbf{r} - \mathbf{r}_1|) \tilde{\phi}_{1S}(|\mathbf{r} - \mathbf{r}_4|) \varphi_{2S}(\mathbf{r}_4) \varphi_{2S}(\mathbf{r}_1) \\
 & \times \left[\int \left(\frac{e^2}{|\mathbf{r}_4 - \mathbf{r}_2|} - \frac{e^2}{|\mathbf{r} - \mathbf{r}_2|} \right) \varphi_{1S}^2(\mathbf{r}_2) d\mathbf{r}_2 + \int \left(\frac{e^2}{|\mathbf{r}_4 - \mathbf{r}_3|} - \frac{e^2}{|\mathbf{r} - \mathbf{r}_3|} \right) \varphi_{1S}^2(\mathbf{r}_3) d\mathbf{r}_3 \right]. \quad (2.15)
 \end{aligned}$$

The two terms of the second part give equal contribution, and obviously modify the effective interaction, by correcting the factor 3 for nuclear charge. They serve to screen out the nuclear potential when the electron in the $2s$ shell is far out. For evaluating the various terms, we shall use the Li atomic wave functions as given by Wilson¹³:

$$\phi_{1S} = \left(\frac{\xi^3}{\pi a_0^3} \right)^{1/2} \exp(-\xi r/a_0), \quad \xi = 2.69a_0; \quad (2.16)$$

$$\phi_{2S} = \frac{1}{(39.089\pi a_0^3)^{1/2}} (1.345r e^{-0.665r} - e^{-1.5r}). \quad (2.17)$$

Using (2.16), the potential

$$\int \frac{e^2}{|\mathbf{r}_4 - \mathbf{r}_2|} \varphi_{1S}^2(\mathbf{r}_2) d\mathbf{r}_2 = \frac{e^2}{r_4} - e^2 \exp(-2\xi r_4/a_0) \left(\frac{\xi}{a_0^2} + r_4^{-1} \right). \quad (2.18)$$

Hence J_1 can be written as

$$\begin{aligned}
 J_1 = & \int d\mathbf{r} d\mathbf{r}_1 d\mathbf{r}_4 \tilde{\phi}_{1S}(|\mathbf{r} - \mathbf{r}_1|) \tilde{\phi}_{1S}(|\mathbf{r} - \mathbf{r}_4|) \varphi_{2S}(\mathbf{r}_4) \varphi_{2S}(\mathbf{r}_1) \\
 & \times \left[e^2(r^{-1} - r_4^{-1}) + \left(\frac{e^2}{|\mathbf{r}_4 - \mathbf{r}_1|} - \frac{e^2}{|\mathbf{r} - \mathbf{r}_1|} \right) - 2e^2 \exp(-2\xi r_4/a_0) \left(\frac{\xi}{a_0^2} + r_4^{-1} \right) + 2e^2 \exp(-2\xi r/a_0) \left(\frac{\xi}{a_0^2} + r^{-1} \right) \right]. \quad (2.19)
 \end{aligned}$$

The last two terms are simply the screening corrections due to the occupied $1s$ orbital. They are exponentially damped out. The long-range part of the $2s$ wave function alone is of importance, hence these terms will be negligible.

The evaluation of (2.19) is analytically possible by the method shown in the Appendix, but the calcu-

lation becomes extremely tedious. The numerical value of the first four terms is

$$J_1' = -2\pi e^2 a_0^2 \times 12.52. \quad (2.20)$$

The correction terms of the exponentials give

$$J_1'' = -2\pi e^2 a_0^2 \times 0.310, \quad (2.21)$$

so that

$$J_1 = -2\pi e^2 a_0^2 \times 12.83. \quad (2.22)$$

Let us now return to the remaining two terms of (2.14).

$$J_2 = \int d\mathbf{r} d\mathbf{r}_1 d\mathbf{r}_4 \tilde{\phi}_{1S}(|\mathbf{r}-\mathbf{r}_1|) \tilde{\phi}_{1S}(|\mathbf{r}-\mathbf{r}_4|) \phi_{1S}(r_1) \phi_{2S}(r_4) \\ \times \int d\mathbf{r}_2 \left(\frac{e^2}{|\mathbf{r}_4-\mathbf{r}_2|} - \frac{e^2}{|\mathbf{r}-\mathbf{r}_2|} \right) \phi_{1S}(r_2) \phi_{2S}(r_2), \quad (2.23)$$

$$J_4 = \int d\mathbf{r} d\mathbf{r}_1 d\mathbf{r}_4 \tilde{\phi}_{1S}(|\mathbf{r}-\mathbf{r}_1|) \tilde{\phi}_{1S}(|\mathbf{r}-\mathbf{r}_4|) \phi_{1S}(r_4) \phi_{2S}(r_1) \\ \times \int d\mathbf{r}_2 \left(\frac{e^2}{|\mathbf{r}_4-\mathbf{r}_2|} - \frac{e^2}{|\mathbf{r}-\mathbf{r}_2|} \right) \phi_{1S}(r_2) \phi_{2S}(r_2). \quad (2.24)$$

Numerically, we find

$$J_2 = -2\pi e^2 a_0^2 \times 0.024, \\ J_4 = 2\pi e^2 a_0^2 \times 0.336. \quad (2.25)$$

Adding (2.22) and (2.25) with appropriate signs,

$$J = -2\pi e^2 a_0^2 \times 13.15. \quad (2.26)$$

Clearly the overwhelming contribution came from (2.20). The remaining terms amount to only a correction of 6%.

We have also carried out the numerical calculation with another set of wave functions for Li given by Zener and Guillemin¹⁴ (unnormalized):

$$u_{1S} = e^{-2.688r}, \\ u_{2S} = (r-0.18)e^{-0.630r}. \quad (2.27)$$

The result is

$$J = -2\pi e^2 a_0^2 \times 15.82. \quad (2.28)$$

Since the Born-approximation result overestimates the cross section, the Wilson wave function value (2.26) is preferred. The conversion-scattering cross section in Li thus comes out to be

$$\sigma = 4\pi a_0^2 \times (13.15)^2. \quad (2.29)$$

For liquid ammonia in the temperature range -77°C to -33.5°C the thermal velocity of the positronium is given by ($T=200^\circ\text{K}$)

$$\frac{1}{2}2mv^2 = \frac{3}{2}kT = 0.016 \text{ eV},$$

or

$$v = 4.34 \times 10^6 \text{ cm/sec.} \quad (2.30)$$

¹⁴ V. Guillemin and C. Zener, Z. Physik 61, 199 (1930).

Hence the σv product of interest in calculating the rate according to Eq. (2.1) is

$$\sigma v = 4.34 \times 10^6 \times 4\pi a_0^2 \times (13.15)^2 = 2 \times 10^{-9} \text{ cm}^3/\text{sec}, \quad (2.31)$$

which is of the correct order of magnitude.

The quenching rate in pure ammonia is known to be $1/\tau_2 = 4.5 \times 10^8 \text{ sec}^{-1}$. To obtain a decay rate 10^8 sec^{-1} , we thus need a concentration

$$10^8 = n \cdot 2 \times 10^{-9},$$

or

$$n = 0.5 \times 10^{17} \text{ per cc.} \quad (2.32)$$

Since the density of liquid ammonia is 0.68 gm/cm^3 at the boiling point -33.5°C , the concentration necessary for a paramagnetic quenching-decay rate 10^8 sec^{-1} is $(0.5 \times 10^{17}) / (2.4 \times 10^{22})$ or 0.21×10^{-5} . This requires a very dilute solution of ammonia.

Since the experiments have to be carried out at various concentrations, it is necessary to know the limitations of the linear formula of Eq. (2.1). One must start considering coherent scattering by pairs of alkali atoms when the de Broglie wavelength of positronium becomes comparable to the average spacing between two alkali atoms. At 200°K , the de Broglie wavelength of positronium is $1.41 \times 10^{-7} \text{ cm}$ or $27 a_0$. The concentration of alkali atoms for such an average spacing is

$$n = \frac{3}{4\pi} \times (1.41)^{-3} \times 10^{+21} = 8 \times 10^{19} \text{ per cc.} \quad (2.33)$$

Another relevant length is the apparent size of the scatterer as represented by the cross section (2.29). The apparent radius comes out to be $26.3 a_0$, so that the concentration where impurities begin to overlap is again $\sim 10^{19} \text{ per cm}^3$. At very high concentrations when the solution begins to show metallic conductivity, there would be no long-lifetime component at all, as indicated by the experiment of Hogg *et al.*⁷ for saturated solutions. When metallic character is present the positronium formation itself is not possible.

However, if one uses a concentration 10^{18} or 10^{19} per cc in (2.1) with our value of σv , it would follow that the decay rate is comparable to or more than the free annihilation rate. Hence at such concentrations 0.1% or so, the long-lifetime component would be absent. This seems to be in agreement with the experimental data of Varlashkin and Stewart.

III. A SIMPLE MODEL

The calculations of the various integrals in Sec. II suggest that the entire effect of quenching can be ascribed to the outermost electron of the alkali atoms,

TABLE I. Computational results. The third column represents the calculation with the simple exponential of the type (3.2). The fourth column gives more accurate results.

Atom	E_i^a (eV)	$-J/2\pi e^2 a_0^2$	$-J/2\pi e^2 a_0^2$
Li	5.39	6.76	13.15
Na	5.14	6.95	(14.6)
K	4.34	7.63	
Rb	4.18	7.77	
Cs	3.89	8.07	
H	13.6	3.75 ^b	3.75 ^b

^a C. Candler, *Atomic Spectra and the Vector Model* (Hilger and Watts, Ltd., London, 1964).

^b This value was obtained by us evaluating the hydrogenic integrals of Massey and Mohr by the method indicated in the Appendix.

at least if we restrict ourselves to the Born approximation. Even the independent-particle approach we used for treating the Li atom becomes prohibitively difficult for other alkali atoms. However, the structure of the dominant term is quite clear, and the problem is reduced to calculating the following integral:

$$J = \int \tilde{\phi}_{1S}(|\mathbf{r}-\mathbf{r}_2|) \psi(r_2) \left[\frac{e^2}{r} - \frac{e^2}{r_1} + \frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|} - \frac{e^2}{|\mathbf{r}-\mathbf{r}_2|} \right] \times \tilde{\phi}_{1S}(|\mathbf{r}-\mathbf{r}_1|) \psi(r_1) dr dr_1 dr_2. \quad (3.1)$$

This has the same structure as the hydrogenic integral,⁴ except that the wave function ψ that appears is the outermost alkali orbital. It turns out that (3.1) is somewhat sensitive to the actual wave function used for $\psi(r)$, in particular the tail of the wave function must be accurately described.

The inner part of the wave function ψ is not of any importance. The simplest way of characterizing the wave function one could think of is to write

$$\psi(r) = (\alpha^3/\pi)^{1/2} e^{-\alpha r}. \quad (3.2)$$

The parameter α is determined from the ionization energy E_i :

$$\hbar^2 \alpha^2 / 2m = E_i. \quad (3.3)$$

J can then be evaluated as before and the results are collected in Table I. In the fourth column we have the result of our detailed calculation of lithium. The value for sodium was obtained by replacing ψ in (3.1) with a two-parameter fit to the atomic 3s wave function of sodium,¹⁵ which reproduced the external part of the wave function accurately.

We notice that the result of using the simple exponential is almost a factor of 2 smaller. Comparing the

wave function (3.2) with α determined by (3.3),

$$\psi(r) = [(0.630)^{3/2} / (\pi a_0^3)^{1/2}] e^{-0.630r}, \quad (3.4)$$

with the Wilson wave function (2.17) we notice that the Wilson wave function lies substantially higher than Eq. (3.4) in the outer region (Fig. 1). This is simply a result of the factor r multiplying the exponential which weights the external region more than in (3.4). It seems, however, that numerical evaluation of (3.1) with $\psi(r)$ being the exact relevant atomic wave function of the alkali atom would be a good approximation to calculating the quenching rate. This is certainly true of Li as Sec. II demonstrates. Also the value in sodium in the fourth column seems to be following the correct trend as in the third.

IV. CONCLUSION

We have shown that a relatively simple calculation can explain the paramagnetic quenching effect of lithium and sodium added to ammonia. On the other hand, we have so far made no serious attempt to justify the use of the Born approximation; this justification is necessary particularly in view of the presence of rearrangement collisions. An extension of our calculation to higher concentrations is possible, following the treatment of Van Hove¹⁶ for slow neutron scattering. This may be necessary when more experimental data are available at concentrations where the long lifetime is almost completely quenched. This is an interesting region both experimentally and theoretically, because of its bearing on the onset of the metallic behavior of alkali atoms. We hope to pursue calculations of the other complex quenching processes and for the long lifetime τ_2 itself.

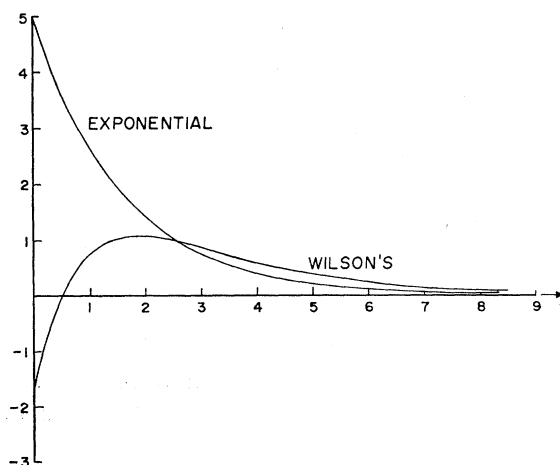


FIG. 1. $(\pi a_0^3)^{1/2} \psi(r)$ plotted against r (in atomic units) for the exponential in Eq. (3.4) and Wilson's 2s wave function in Eq. (2.17).

¹⁵ E. Kennard and E. Ramberg, *Phys. Rev.* **46**, 1034 (1934).

¹⁶ L. Van Hove, *Phys. Rev.* **95**, 249 (1954).

APPENDIX

All the integrals that appear in the calculations in the zero-momentum-transfer limit have essentially similar structure. It will be enough to illustrate the calculation of one of them. Considering one term of (3.1) with $\psi = \varphi_{1S}$,

$$I = e^2 \int \tilde{\phi}_{1S}(|\mathbf{r}-\mathbf{r}_2|) \phi_{1S}(\mathbf{r}_1) r_1^{-1} \times \tilde{\phi}_{1S}(|\mathbf{r}-\mathbf{r}_1|) \phi_{1S}(\mathbf{r}_2) d\mathbf{r} d\mathbf{r}_1 d\mathbf{r}_2. \quad (\text{A1})$$

Putting in the appropriate eigenfunctions, and making everything under the integration symbol dimensionless, we get

$$I = \frac{e^2 a_0^2}{8\pi^2} \int r_1^{-1} \exp(-\frac{1}{2}|\mathbf{r}-\mathbf{r}_1|) \exp(-r_1) \times \exp(-\frac{1}{2}|\mathbf{r}-\mathbf{r}_2|) \exp(-r_2) d\mathbf{r} d\mathbf{r}_1 d\mathbf{r}_2. \quad (\text{A2})$$

a_0 is the Bohr radius. Similar exponentials appear in various combinations in the integrals. Consider now ($\alpha = \frac{1}{2}, \beta = 1$)

$$I_1 = \int r_1^{-1} \exp(-\alpha|\mathbf{r}-\mathbf{r}_1|) \exp(-\beta r_1) d\mathbf{r}_1 \quad (\text{A3}) \\ = 2\pi \int_0^\infty dr_1 r_1 \exp(-\beta r_1) \\ \times \int_{-1}^{+1} \exp[-\alpha(r^2+r_1^2-2r r_1 x)^{1/2}] dx. \quad (\text{A4})$$

Putting $r^2+r_1^2-2r r_1 x = l^2$, we reduce the second part:

$$\int_{-1}^{+1} dx \exp[-\alpha(r^2+r_1^2-2r r_1 x)^{1/2}] \\ = -\frac{1}{r r_1} \left[\exp[-\alpha(r+r_1)] \left(\frac{r+r_1}{\alpha} + \frac{1}{\alpha^2} \right) \right. \\ \left. - \exp(-\alpha|r-r_1|) \left(\frac{|r-r_1|}{\alpha} + \frac{1}{\alpha^2} \right) \right], \quad (\text{A5})$$

so that integral I_1 is expressed in terms of elementary integrals;

$$I_1 = 2\pi \left[\frac{e^{-\beta r}}{r} A_1 + \frac{e^{-\alpha r}}{r} A_2 + e^{-\alpha r} A_3 \right], \quad (\text{A6})$$

where

$$A_1 = [\alpha(\alpha+\beta)]^{-1} (\alpha^{-1} + (\alpha+\beta)^{-1}) \\ - [\alpha(\beta-\alpha)]^{-1} (\alpha^{-1} - (\beta-\alpha)^{-1}), \\ A_2 = -A_1, \\ A_3 = \alpha^{-1} ((\beta-\alpha)^{-1} - (\beta+\alpha)^{-1}). \quad (\text{A7})$$

To integrate the other part of I of Eq. (A2), take

$$I_2 = \int \exp(-\alpha|\mathbf{r}-\mathbf{r}_2|) \exp(-\beta r_2) d\mathbf{r}_2. \quad (\text{A8})$$

We notice

$$I_2 = -\partial I_1 / \partial \beta, \quad (\text{A9})$$

so that

$$I_2 = 2\pi \left[\frac{e^{-\beta r}}{r} B_1 + \frac{e^{-\alpha r}}{r} B_2 + e^{-\beta r} B_3 + e^{-\alpha r} B_4 \right], \quad (\text{A10})$$

with

$$B_1 = \frac{1}{\alpha(\alpha+\beta)^2} \left(\alpha^{-1} + \frac{2}{\alpha+\beta} \right) - \frac{1}{\alpha(\beta+\alpha)^2} \left(\alpha^{-1} - \frac{2}{\beta-\alpha} \right), \\ B_2 = -B_1, \quad B_3 = A_1, \\ B_4 = \alpha^{-1} \left(\frac{1}{(\beta-\alpha)^2} - \frac{1}{(\beta+\alpha)^2} \right). \quad (\text{A11})$$

Hence Eq. (A2) gives

$$I = 2\pi e^2 a_0^2 \int_0^\infty r^2 dr I_1 I_2 \\ = 2\pi e^2 a_0^2 \left[\frac{A_1 B_1}{2\beta} + \frac{A_1 B_3}{(2\beta)^2} + \frac{A_1 B_2 + A_2 B_1}{\alpha + \beta} \right. \\ \left. + \frac{A_1 B_4 + A_2 B_3 + A_3 B_1}{(\alpha + \beta)^2} + \frac{2A_3 B_3}{(\alpha + \beta)^3} \right. \\ \left. + \frac{A_2 B_2}{2\alpha} + \frac{A_2 B_4 + A_3 B_2}{(2\alpha)^2} + \frac{2A_3 B_4}{(2\alpha)^3} \right], \quad (\text{A12})$$

where we have used

$$\int_0^\infty e^{-\lambda n} n^n dn = n! / \lambda^{n+1}. \quad (\text{A13})$$

For $\alpha = \frac{1}{2}, \beta = 1$, we then get $I_1 = 2\pi e^2 a_0^2 \times 10.1$. Equation (A5) is the important step in every other integral.