Regarding Covariant Subtraction of Infinities[1]

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It has been brought out by Pauli and Villars (*1*) that requirements of covariance are not sufficient to determine physical answers in the Tomonaga-Schwinger (*2*) formulation of quantum electrodynamics, and that the indefiniteness of the theory is caused by the indeterminateness of the four dimensional Δ-functions. Pauli and Villars (*1*) show that by formal regularization the results may be changed within wide limits. A few remarks may be permitted concerning this feature of the theory.

1. There is a close relationship between the Dirac-Fock-Podolsky (*3*) formulation and the new one, as has been emphasized by Tomonaga (*1*). The new formalism differs from the DFP formulation mainly through the employment of quantized matter waves. In the DFP theory the supplementary condition has the form

$$[\text{div } \mathbf{A} + \partial\Phi/c\partial t - \Sigma\varepsilon_s\Delta(X - X_s)/4\pi]\psi = 0,$$

where $\mathbf{A}$, ϕ are the vector and scalar potentials, ϵ_s are the charges, X and X_s designate respectively the four dimensional field and particle positions. The function Δ is 4 π times Schwinger's D. It is well known that the above equation of constraint contains singularities, as is especially clear in its consequence

$$\{\text{div } \mathbf{E} + (\partial/c\partial t)\Sigma(\varepsilon_s/4\pi)\Delta(X - X_s)\}\psi = 0,$$

and the corresponding formulas for $\partial\mathbf{E}/c\partial t$. The above comparison shows that one can hardly expect unique predictions without a precise specification of the averaging process employed in dealing with the Δ or D functions.

2. The Pauli-Jordan invariant Δ function has been extended by Dirac (*4*) so as to include cases with non-vanishing mass. Whereas Schwinger's (*1*) treatment is more symmetric regarding space-time, the explicit character of Dirac's work has advantages. One can verify, following Dirac's calculation, that for $\lambda > 0$

$$\overline{\Delta} = [\delta(\lambda)/4\pi] - (\kappa_0^2/8\pi)J_1(\kappa_0\lambda^{1/2})/(\kappa_0\lambda^{1/2}),$$

where

$$\lambda = -r^2 + x_0^2,$$

in agreement with Schwinger. One has also

$$\overline{\Delta} = -(\partial/8\pi r\partial r)F(\kappa r, \kappa_0 x_0),$$

where

$$F(\kappa_0 r, \kappa_0 x_0) = J_0(\kappa_0\lambda^{1/2}) \ (\lambda > 0)$$
$$= 0 \ (\lambda < 0).$$

The function F has a discontinuity on the light cone. The introduction of $\Delta = -2(x_0/|x_0|)\overline{\Delta}$ removes the discontinuity in its surface integral, but the discontinuity of F remains.

A natural but nevertheless arbitrary way of removing the singularity is to consider the δ functions in

$$(\Box - \kappa_0^2)\overline{\Delta}(x) = -\delta(x_0)\delta(\mathbf{r}),$$

as defined in the sense of being the limit of a family of nonsingular functions obtainable, e.g., by first Fourier-analyzing and then proceeding to the limit in the space of the wave number $k/2\pi$ of this analysis by integrating from $-N$ to $+N$ and making $N \to \infty$.

3. Although, according to Pauli and Villars, one cannot claim that the Tomonaga-Schwinger attempt derives its results from general principles, it is also true that the intuitive methods of calculation agree with experiment. The addition of a hypothesis that invariant Δ functions should be first replaced by a Fourier Integral, which should next be replaced by a similar integral with finite limits of integration (or infinite limits but with a weighting factor), is admittedly arbitrary. Such a procedure is closely related, however, to Heisenberg's convergent theory (*5*) of elementary particles, in which an elementary length is introduced in virtue of the elementary interaction. The commutation relations are here nonsingular, and the formulation adapts itself to a Fourier representation. One may expect, therefore, that for lengths large compared with Heisenberg's elementary length the consequences will be similar to those obtainable from the TSFD developments, with the addition of a postulate concerning the method of evaluation of divergent expressions along the lines carried out in Schwinger's papers. The weighting factor should then appear in an approximation neglecting phenomena within the elementary length. The symmetry in the treatment of the Fourier representations may be expected to arise through the virtual creation of other than the interacting particles. Since the creation takes place in the region of space-time containing the singularity of the TSFD discussions which corresponds, e.g., to $\lambda = 0$ in equation (2.33) of Schwinger's second paper of the series quoted, the Δ functions of the TSFD theory will be modified for large k. The writer believes, therefore, that future theories will agree in the limit of large lengths with the (k) representation and its symmetric calculation.

The introduction of symmetry requirements for the magnetic moment problem occurs in Schwinger III in the evaluation of the logarithmically divergent integral occurring in equation (1.103) for $n = 0$. The invariant minimum light quantum number associated with the infrared catastrophe is introduced in his equation (1.107) and the Fourier representations in equation (1.66). The operation would be impossible without the physical identification made in equation (1.106). The related discussion in the Appendix is in terms of the k representation of the singular functions. In the discussion of vacuum polarization similar steps

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occur in relation to equation (2.36) and (2.39) of Schwinger II.

It may be argued that ordinary space-time is as good as (k) space. But the occurrence of new particles appears more directly in the latter on account of the connection with energy and momentum. The effect is as though "elementary particles" had a size, as has been brought out by Heisenberg (*5*).

References

1. PAULI, W., and VILLARS, F. *Rev. Modern Phys.*, **21**, 434 (1949).
2. TOMONAGA, S. *Progress Theor. Phys.*, **1**, 27 (1946); KOBA, TATI, and TOMONAGA. *Ibid.*, **2**, 101, 198 (1947); KANESAWA, S., and TOMONAGA, S. *Ibid.*, **3**, 1, 101 (1948); TOMONAGA, S. *Phys. Rev.*, **74**, 224 (1948); SCHWINGER, J. *Ibid.*, 1439; *ibid.*, **75**, 651 (1948); *ibid.*, **76**, 790; FEYNMAN, R. P. *Ibid.*, **74**, 939 (1948); *ibid.*, 1430; *ibid.*, **76**, 749 (1949); *ibid.*, 769; DYSON, F. J. *Phys. Rev.*, **75**, 486 (1949).
3. DIRAC, P. A. M., FOCK, V. A., and PODOLSKY, B. *Phys. Z. Sowjunion*, **2**, 468 (1932). (In referring to the equations in this and other papers the notation of the reference quoted is used here.)
4. DIRAC, P. A. M. *Proc. Cambridge Phil. Soc.*, **30**, 150 (1934).
5. HEISENBERG, W. *Z. Naturforsch.*, **5a**, 251 (1950); *ibid.*, 367.

Nonclassical Reaction Kinetics

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Barrier leakage was early invoked by Gamow and by Condon and Gurney to explain nuclear decomposition. For particles of mass m, position X, and energy E_i in the ith state, moving on a potential energy surface $V(X)$, the specific reaction velocity, v, (or frequency of passing a smooth energy barrier ($E_i < V$) which occupies the region ($X_1 \leq X \leq X_2$)) may be written:

$$v = \sum_i n_i \nu_i \gamma_i = 4 \sum_i n_i \nu_i \exp \left(- \frac{2\sqrt{2m}}{\hbar} \int_{X_{1i}}^{X_{2i}} \sqrt{V(X) - E_i}\, dX \right), \qquad (1)$$

where n_i, ν_i, and γ_i are the fractional population of the ith level, the frequency of vibration normal to the reaction barrier, and the probability of barrier penetration per encounter, respectively. Because of the flatness of barriers in ordinary chemical reactions, leakage is usually negligible in comparison to the surmounting of barriers. The inversion of the ammonia pyramid is one of a small group of interesting exceptions that are reasonably well understood.

Hardness, electrical resistivity, and magnetism of metals, when treated as rate processes, provide added examples of nonclassical kinetics. Application of the classical expression for the net specific rate k'_{net} of surmounting barriers

$$k'_{\text{net}} = \frac{2\kappa kT}{h} \exp \left(- \frac{\Delta F^{\ddagger}}{RT} \right) \sinh \frac{V \cdot \sigma}{2kT} \qquad (2)$$

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to plastic flow of metals by Fredrickson and Eyring (*1*) and Kauzmann (*2*) led to a free energy of activation $\Delta F^{\ddagger}$ proportional to the temperature (a pure entropy) and $\frac{V_h}{2kT}$ independent of the temperature. V_h, with the dimensions of volume, is the area of the slipping unit in the plane of slip times the mean distance traveled per slip. That V_h should be proportional to the temperature is not impossible, but scarcely to be anticipated (*3*).

It seems more natural to replace the classical equation (2) for plastic flow by the appropriate extension (1), from which the observed temperature effect follows easily. In this case, the effective potential $V(X)$ is reduced at each point along the barrier by a small amount $a\sigma$, against motion of the particles in the direction to relax the stress σ; and is raised by a similar amount against return to the initial state, once the barrier has been passed. This is to be understood in terms of the distortion of the average electrostatic field by a relative displacement of the mean positions of atomic kernels. Expanding the radical in equation (1) to the first order in powers of $a\sigma$ (the correction to V) and replacing the sum by a single "average" term, we obtain for the excess velocity in the direction to relieve stress over that of return

$$v_{\text{net}} = 8\bar{\nu} \exp(-\bar{g}\bar{m}p) \sinh(\bar{b}\bar{m}p\sigma), \qquad (3)$$

where

$$\bar{g} = \frac{2\sqrt{2\bar{m}}}{\hbar} \int_{X_{1i}}^{X_{2i}} \sqrt{V - E_i}\, dX, \quad \bar{b} = \frac{|2\bar{m}}{\hbar} \int_{X_{1i}}^{X_{2i}} \frac{a\,dX}{\sqrt{V - E_i}},$$

and $\bar{m}$ and p will be discussed shortly.

Equation (3) must be interpreted as follows: Crystal geometry permits slip only through the cooperation of $\bar{m}$ neighboring atoms. At moderate temperatures these atoms may be treated as independent oscillators, as in the Einstein theory of specific heats. $\bar{\nu}$ is the effective frequency of vibration of the normal mode along the slip plane. These electrons must each penetrate the electrostatic barriers separating initial and final configurations if slip is to occur. For independent atom vibrations, normal to the slip plane factors relating to the individual probabilities of penetration must be raised to a power $\bar{m}p$, where p is the average number of exterior electrons on each atom. The electronic integrals are to be averaged over the atomic vibrations, where the energies and limits of integration depend upon atomic coordinates. Except for temperature dependence, equation (3) has the same behavior as (1), the validity of which has already been studied.

This formalism also makes clear the effect of large amounts of alloy elements on plasticity. Since the local regions of slip are considerably less orderly than the perfect crystal, in the first approximation atomic interactions can be considered to take place between pairs of neighboring atoms. If x is the atomic fraction of constituent A, and $(1-x)$ that of B, then evidently for alloys $p\bar{g}$ takes the form