

There is no evidence of a maximum near the threshold, although this possibility is not excluded.

The resolution of the mass separator was sufficient to exclude O_2^- , which has a detachment threshold below 1 volt and a cross section of about 0.4×10^{-18} cm² at 8000 Å. Mass peaks of impurities at 17 and 19 amu were about 0.2 percent of the $(O^{16})^-$ peak, and thus comparable with the $(O^{18})^-$ peak, as determined with a high-resolution analyzer after the detachment chamber.

The O^- affinity given by our data is 1.45 ± 0.15 eV, the estimated uncertainty being related to the shape of $\sigma(\lambda)$ very near the threshold. This result is in unresolved conflict with previous experiments,¹⁻⁶ although not inconsistent with theoretical extrapolations.

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Orthogonality of the Furry-Sommerfeld-Maue Wave Functions and their Use in Perturbation Theory

ROBERT T. SHARP AND J. DAVID JACKSON

Department of Mathematics, McGill University, Montreal, Canada

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IN a recent paper on internal pair formation, Horton and Phibbs¹ assert that the Furry-Sommerfeld-Maue wave functions²⁻⁴ for a Dirac particle in a Coulomb field are not orthogonal, and that for any process calculated by perturbation theory using these wave functions, the interaction matrix element must be modified accordingly.

It is our contention that the Furry-Sommerfeld-Maue wave functions are orthogonal in the usual sense, at least to the order of magnitude to which they are valid, and that perturbation theory does not need to be modified in any way on account of their use.

Horton and Phibbs prove in their Appendix I that the wave function of a positive electron with energy E_+ which satisfies the iterated Dirac equation with a Coulomb potential is not orthogonal to the wave function of a negative electron with energy E_- which satisfies a similar iterated equation. This is to be expected, since the positive and negative electrons have different Hamiltonians, the Coulomb terms being of opposite signs. As will be seen below, the lack of orthogonality of wave functions appropriate to different Hamiltonians is irrelevant to the problem.

In their Sec. III Horton and Phibbs go through the

standard derivation of time-dependent perturbation theory, but because of the assumed applicability of their Appendix I, end up with a modified interaction matrix element [their Eqs. (16) and (18)]. The results of their Appendix I are not applicable, however, because, as is customary, they use as their unperturbed wave functions the various eigenfunctions of a *single* Hamiltonian. In the pair production problem, this demands interpreting the initial state as that of a negative electron with negative energy and the final state as that of a negative electron of positive energy.⁵ Horton and Phibbs make the error of identifying the initial state wave function with that of a positive electron of positive energy satisfying the iterated Dirac equation, and so are led to use the irrelevant Appendix I to alter perturbation theory.

It is a straightforward matter to show that for a given sign of the electronic charge, wave functions satisfying both the ordinary and iterated Dirac equations of two different energies are orthogonal in the usual sense. Since the Furry-Sommerfeld-Maue wave functions are approximate solutions of these equations, they will be orthogonal to the same order of approximation. Consequently no modification of perturbation theory is necessary when these wave functions are used.

It should be mentioned that the main conclusions of Horton and Phibbs on the validity of the Born approximation in internal pair production are unaffected.

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⁵ See Sec. V of reference 4 for this argument applied directly to the Furry-Sommerfeld-Maue wave functions.

Comments on Straumanis' Concepts Regarding Avogadro's Number*

E. RICHARD COHEN, *North American Aviation, Inc., Downey, California*

AND

J. W. M. DUMOND, *California Institute of Technology, Pasadena, California*

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STRAUMANIS¹ has advocated that Avogadro's number be defined in terms of a standard crystal, "purest calcite," until such time as a "truly reliable" value may be established. This suggestion introduces a new variable into the field of the atomic constants: the ratio of the true value to the standard value. Although his proposal is based on a consideration of operational definitions for physical quantities, it is not in accord with the philosophy of simplification of concepts. It is, however, strongly influenced by the existence of discrepancies in the values obtained for Avogadro's number (both by direct measurement and

by indirect inference from least-squares adjustments, such as those of DuMond and Cohen²). We have pointed out³ that, in contradiction to Straumanis, there are several experimental methods which yield values of Avogadro's number more accurate than the direct crystal density method. In a rebuttal⁴ Straumanis countered with the argument that the crystallographer was concerned primarily with the quantity which we might call the Siegbahn-Avogadro number rather than with N itself. The Siegbahn-Avogadro number is defined here as $N_s' = N(\lambda_g/\lambda_s)^3$, and is the actual quantity which results from the direct crystal density x-ray method.⁵ It is N_s' , and not N , which relates macroscopic density, molecular weight, and lattice spacing in x-units.

The crystallographer, using these units, is therefore interested in finding the experimental procedure which gives N_s' with highest accuracy, rather than the one which gives the most accurate value of N . Although DC 54³ showed that the indirect methods can give the most accurate value of N , it is also true that, in general, they give N_s' with lesser accuracy. It is therefore useful to compare the direct value of N_s' with the indirect values computed from measurements of other physical constants.

We shall use the data given in DC 54 and shall use essentially the same notation as that paper. The equations of DC 54, each identified by a description of the experiments which it represents, are

$$\begin{array}{rcl} x_3 + x_4 & = & 84.2 \pm 10.9 = a_1 \quad (\text{Faraday constant}), \\ -3x_1 + 2x_3 + x_4 & = & 145.0 \pm 10.5 = a_2 \quad (\text{proton cyclotron resonance}), \\ 3x_1 - x_3 & = & -23.0 \pm 22.9 = a_3 \quad (\text{proton magnetic resonance}), \\ & & x_5 = 0.0 \pm 30.1 = a_4 \quad (\text{grating wavelengths}), \\ -x_1 + x_3 - x_5 & = & -65.4 \pm 29.5 = a_5 \quad (\text{short-wavelength limit}), \\ & & x_4 + 3x_5 = 34.0 \pm 37.8 = a_6 \quad (\text{x-ray crystal density}), \\ x_1 & = & 40.0 \pm 4.5 = a_7 \quad (\text{hydrogen fine structure}). \end{array}$$

We now introduce into these equations the substitution $y = x_4 + 3x_5$, so that y is the linearized variable corresponding to $N(\lambda_g/\lambda_s)^3$. In addition to the direct value, a_6 , the other six equations can be combined into eleven distinct just-determinate solutions. Listed in the order of their accuracy, the complete set of solutions is

$$\begin{array}{ll} a_6 & N(\lambda_g/\lambda_s)^3 = (0.606179 \pm 0.000023) \times 10^{24} \\ a_1 + 2a_4 - a_5 - a_7 & N(\lambda_g/\lambda_s)^3 = (0.606225 \pm 0.000023) \times 10^{24} \\ a_2 + a_4 - 2a_5 + a_7 & N(\lambda_g/\lambda_s)^3 = (0.606350 \pm 0.000036) \times 10^{24} \\ \frac{1}{2}(a_1 - a_2 + 3a_4 - 3a_5) & N(\lambda_g/\lambda_s)^3 = (0.606276 \pm 0.000039) \times 10^{24} \\ \frac{1}{2}(a_1 + a_2 + 3a_4 - 3a_5) & N(\lambda_g/\lambda_s)^3 = (0.606287 \pm 0.000039) \times 10^{24} \\ \frac{1}{2}(2a_2 + a_3 + 3a_4 - 3a_5) & N(\lambda_g/\lambda_s)^3 = (0.606299 \pm 0.000040) \times 10^{24} \\ -a_1 + 2a_2 - 3a_5 + 3a_7 & N(\lambda_g/\lambda_s)^3 = (0.606475 \pm 0.000056) \times 10^{24} \\ a_2 - a_3 - 3a_5 + 3a_7 & N(\lambda_g/\lambda_s)^3 = (0.606452 \pm 0.000057) \times 10^{24} \\ a_1 + a_3 + 3a_4 - 3a_7 & N(\lambda_g/\lambda_s)^3 = (0.606122 \pm 0.000058) \times 10^{24} \\ 2a_1 - a_2 + 3a_4 - 3a_7 & N(\lambda_g/\lambda_s)^3 = (0.606099 \pm 0.000058) \times 10^{24} \\ a_1 - 2a_3 - 3a_5 + 3a_7 & N(\lambda_g/\lambda_s)^3 = (0.606428 \pm 0.000061) \times 10^{24} \\ a_2 + 2a_3 + 3a_4 - 3a_7 & N(\lambda_g/\lambda_s)^3 = (0.606145 \pm 0.000062) \times 10^{24} \end{array}$$

The least-squares solution is 0.606208 ± 0.000020 (the error is the standard deviation by internal consistency; it becomes 0.000050 by external consistency). We see that the solutions range from a high 0.606475 to a low of 0.606099 , whereas the direct value (which is the most accurate solution of the set) is 0.606179 ± 0.000023 . The second solution of the set is statistically as accurate as the direct measurement, yet the two values disagree by approximately 1.5 times the error of the difference. The failure of the standard deviation spread of the direct value to contain a single one of the set of the other (indirect) values, whereas one would expect it to contain on the order of half of them, is indicative of the type of discrepancy with which we are faced.

Straumanis is therefore correct in stating that the crystal density x-ray diffraction method gives the best single determination of N_s' , although a least-squares adjusted value which is based on an evaluation of

all the pertinent data is presumably more accurate still.

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⁵ The quantity N_s' is a physical constant like N or e , whose value is to be determined by experiment, either directly or indirectly. It is to be distinguished from the number $N_s = 0.60594 \times 10^{24}$ (a specific numerical value) which was deduced by Siegbahn from the Faraday constant and the early (incorrect) "oil drop" value of the electron charge. Siegbahn used N_s as the value of Avogadro's number in a calculation which was originally intended to give the grating space of calcite in centimeters. This value is now regarded instead as *arbitrarily* establishing an *exact* value in x-units. The statement that the effective grating space of calcite for first-order reflection at 18°C is 3029.04 x-units defines this unit. Since Siegbahn's work, the values of the chemical atomic weights have changed slightly, and the perturbing effects of crystal purity have been pointed out by Straumanis and others; the experimental value N_s' is therefore no longer in agreement with the number N_s .