given by (13) depend less strongly on the value assigned to the parameter m than is the case for the $E(1)$ approximations. Moreover, these values are grouped closely around the precise estimate of E/b^4 for a hard-sphere gas, viz. 0.1103 ± 0.0003, recently computed by Ree and Hoover [5]. In particular, if m is chosen so as to make the approximation defined by (7) self-consistent for the virial coefficient D, then the value deduced for E_C is correct; by taking $m = 0.4431$ so as to give D_C the correct value, the estimate of E_C is within 2.5 per cent of the true value; and, corresponding to that value of m (0.4055) which identifies D_p with D, we find $E_C = 0.1089\ b^4$, which is accurate to 1.3 per cent.

Of the eight $E(1)$-type approximations they examined, Hutchinson and Rushbrooke consider the $E''(1)$ 'compressibility' approximation associated with $m = 0.3646$ to be the best. Clearly, provided m is assigned any fixed value within the range $0.4 < m < 0.45$, the present model yields estimates of the pair of virial coefficients D_C and E_C for a hard-sphere gas which are more acceptable than those provided by any of the $E(1)$ approximations. As regards its approach to self-consistency and its ability to produce results for the 'compressibility' virial coefficients which are close to accurate values, the approximation here described appears to be markedly superior to any other of comparable simplicity yet devised.

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THE ELECTRIC DIPOLE MOMENT OF AN ATOM

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Some years ago it was pointed out [1] that the detection of an electric dipole moment in an elementary particle would imply that time-reversal invariance is violated. The possible existence of an electric dipole moment in an elementary particle has assumed new interest with the recent suggestion [2] that CP may be violated in the weak interactions combined with the realisation [3] that the weak interactions through the mediation of the intermediate vector boson can have a much larger effect on electromagnetic phenomena than was previously supposed.

Experimentally, the limit on the electric dipole moment of the neutron [4] is 3×10^{-20} cm $\times e$ where e is the charge on the electron. This limit is very close to the value to be expected [5] if time-reversal is violated in the weak interactions. The corresponding limit on the electric dipole moment of the electron [6] is of order 10^5 larger. The big difference in the limits occurs because it is not possible to carry out on a charged particle such as the electron the very precise resonance experiment which was used for the neutron.

A possible way out of this difficulty is to perform the resonance experiment on an uncharged atom and then attempt to interpret the result in terms of the electric dipole moment of the free electron. At first sight, this approach is not promising. Schiff [7] has given a very powerful theorem which implies that an atom does not have an electric dipole moment even if the electron does. However, this theorem is only true in the non-relativistic limit. We argue in this letter that if relativity is taken into account an atom can have an electric dipole moment and that in the heavy alkalis the electric dipole moment of the atom may be considerably larger than that of the free electron. This result has the important consequence that current experiments [8] on the electric dipole moment of the caesium atom yield a limit on the electric dipole moment of the

electron many orders of magnitude lower than that previously available.

Salpeter [9] has shown how an electric dipole moment can be introduced into the single electron Dirac equation in a Lorentz covariant manner. We assume that we can generalise this for a many electron atom by adding a perturbation term

$$H' = - d_e \sum_i \beta_i \sigma_i \boldsymbol{E}_i \qquad (1)$$

to the unperturbed Hamiltonian

$$H^0 = \sum_i [\beta_i mc^2 + \boldsymbol{\alpha}_i \cdot c\boldsymbol{p}_i - eV_i] + \sum_{j \neq k} \tfrac{1}{2} [\frac{e^2}{r_{jk}} + B_{jk}] \qquad (2)$$

Here, E_i is the total electric field at the ith electron, d_e is the electric dipole moment of the free electron and B_{jk} is the Breit interaction.

Now Schiff's theorem says that the non-relativistic part of the expectation value of H' must vanish. In order to exhibit this in an obvious fashion we re-write H' in the form

$$H' = \frac{d_e}{e} [H_0, \sum_i \sigma_i \cdot \nabla_i] + \frac{d_e}{e} [\sum_i \sigma_i \cdot \nabla_i, \sum_{j \neq k} \tfrac{1}{2} B_{jk}] + \cdot + d_e \sum_i (1 - \beta_i) \sigma_i \cdot \boldsymbol{E}_i \qquad (3)$$

The first term on the right side of (3) does not contribute to the expectation value of H' since it consists of the commutator of an operator with the unperturbed Hamiltonian. The second term does not occur in a non-relativistic theory because it involves the relativistic Breit operator. The final term is also clearly relativistic since $(\beta - 1)$ is an operator which picks out the small component of the single particle wave-function. Thus in the non-relativistic limit the expectation value of H' is zero. However, it need not vanish in general since there will be contributions from both the second and third terms in (3). Preliminary estimates show that the contribution from the Breit operator is small compared to that from the third term. Thus to an adequate approximation the energy due to the electric dipole moment of the electrons is given by

$$W' = d_e \langle \psi_0 | \sum_i (1 - \beta_i) \sigma_i \cdot \boldsymbol{E}_i | \psi_0 \rangle \qquad (4)$$

where ψ_0 is the wave function of the atom in the electric field.

The simplicity of this result is rather deceptive in as much as we are interested in that part of W' which is linear in the strength of an externally applied uniform electric field and this dependence is contained both in the operator and in the wave-function. If we assume that the applied field is small enough that it can be treated as a perturbation on the free atom the linear component of W' takes the form:

$$W' = d_e \langle \phi_0 | \sum_i (\beta_i - 1)(\sigma_i \cdot \nabla_i V_0(i)) | \phi_0 \rangle + \text{cc.} + d_e \langle \phi_0 \sum_i (1 - \beta_i) \sigma_i \cdot \boldsymbol{E}_u | \phi_0 \rangle \qquad (5)$$

Here E_u is the strength of the uniform electric field which is assumed to along the Z direction. $V_0(i)$ is the total potential experienced by the ith electron in the absence of the external electric field. ϕ_p is the first order perturbation of the atomic wave-function ϕ_0 by the electric field.

The accurate evaluation of (5) for an atomic ground state is a formidable problem in relativistic many-electron theory. However, for the alkalis some important simplifications are possible. The very large polarisibility means that the last term in (5) is small compared to the first two and may be neglected. If we assume the usual central-field approximation then ϕ_0 is a single determinant and ϕ_p can differ from ϕ_0 by at most one single particle function. Under these circumstances (5) reduces to simple single particle matrix elements. If we carry out the angular integrations and express the result in terms of the ratio R of the electric dipole moment of the atom to that of the electron we find

$$R = \tfrac{4}{3} \int_0^\infty g_{ns}(r)\, g_p(r) \frac{du(r)}{dr}\, dr$$

where $g_p(r)$ satisfies the relativistic Sternheimer equations

$$[-\frac{d}{dr} + \frac{1}{r}] g_p(r) = \alpha (E_{ns} - U(r)) f_p(r) + \alpha r f_{ns}(r)$$
$$[\frac{d}{dr} + \frac{1}{r}] f_p(r) = [-\frac{2}{\alpha} + \alpha (E_{ns} - U(r))]\, g_p(r) + \alpha r g_{ns}(r). \qquad (9)$$

Here, $f_{ns}(r)$ and $g_{ns}(r)$ are the large and small components of the valence electron wave-function and $U(r)$ is the average potential which is experienced by all the electrons in the central field model.

We have computed R from (8) and (9) using the central potential for caesium given by Hermann and Skillman [10] and we find: $R = 120$. Thus we have the remarkable result that the electric dipole moment of the caesium atom is much larger than that of the electron. A similar enhancement factor has been found by Salpeter [9] in a related calculation on the metastable $2\,s_{\frac{1}{2}}$ state of hydrogen. However, this state is not suitable for an investigation of the electric dipole moment of the electron because the metastability is destroyed by the electric field. In the ground state of hydrogen R is very small

being of the order of 10^{-4}.

The numerical result quoted above can only be regarded as provisional in view of the approximations made in the calculation. However, the enhancement factor R is clearly of the order 100. As we pointed out above this means that current experiments on the electric dipole moment of the caesium atom can be interpreted to yield a limit on the electric dipole moment of the free electron many orders of magnitude lower than that previously available. A more complete calculation will be reported in a forthcoming paper.

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INFORMATION THEORY IN QUANTUM STATISTICAL MECHANICS

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Since the advent of information theory some attempts have been made to relate it to quantum statistical mechanics. In particular it has been suggested [1, 2] that the least biased prediction of properties of a system subject to prior knowledge of the expectation values of a set of observables O_i, $i = 1, 2 \ldots n$, is obtained by use of the maximum entropy density operator, ρ. One obtaines ρ by use of Lagrange multipliers to maximize the information given by $I = -\operatorname{Tr} \rho \ln \rho$ subject to the $n+1$ constraining conditions $\langle O_i \rangle = \operatorname{Tr} \rho\ O_i\ i = 1 \ldots n$ and $\operatorname{Tr} \rho = 1$. No mention has been made of any restrictions on the set of observables O_i, so one is left with the impression that such a treatment is valid for an arbitrary set.

The purpose of this note is to point out that the set of observables is not arbitrary in that at least one observable must have the property that its diagonal matrix elements in the eigenfunction representation of ρ must be monotonic increasing. This was pointed out some time ago for the special case in which the initial constraint, besides $\operatorname{Tr} \rho = 1$, is the value of $\langle H \rangle$ where H is the Hamiltonian [3], but appears to have been overlooked in more general applications.

The necessity of this restriction can be seen by consideration of the expressions for the partition function $Z(\lambda_1 \ldots \lambda_n)$ and the maximum entropy density operator ρ given by [1, 2].

$$Z(\lambda_1 \ldots \lambda_n) = \operatorname{Tr} \left[\exp \left(- \sum_{i=1}^{n} \lambda_i O_i \right) \right] \qquad (1)$$

and

$$\rho = \frac{\exp \left(- \sum_{i=1}^{n} \lambda_i O_i \right)}{Z(\lambda_1 \ldots \lambda_n)} \qquad (2)$$

where the $\lambda_1 \ldots \lambda_n$ are the Lagrange multipliers and the initial constraints consist of the values of $\langle O_i \rangle\ i = 1 \ldots n$. If the eigenfunctions of ρ consist of the basis set $|\alpha)$ which is denumerably infinite, then eq. (1) gives

$$Z(\lambda_1 \ldots \lambda_n) = \sum_{\alpha=0}^{\infty} \exp \left[- \sum_{i=1}^{n} \lambda_i (\alpha | O_i | \alpha) \right]. \qquad (3)$$

Since $\lambda_i \geq 0$ for each i, this sum exists only if

$$(\alpha | O_i | \alpha) < (\alpha + 1 | O_i | \alpha + 1) \qquad (4)$$

for all α for at least one observable in the set.