this accuracy since 3×10^{-4} a.u. of energy is only 8×10^{-3} ev or about 0.2 kcal per mole.

RELATION TO NUMERICAL INTEGRATION

The choice of points and weighting factors is reminiscent of a numerical integration. Although the present method does not depend upon the summations being approximations to integrals, the later possible use of such functions to calculate expectation values of other quantum mechanical quantities would have to depend upon integration. Therefore it is of interest to see how closely a given matrix component defined by a limited summation approaches to the corresponding integral.

As an example of an integral

$$S_{11}=(R^3/8)\int_1^\infty\int_0^1 \exp(-2z\mu)(\mu^2-\nu^2)\,d\mu d\nu,$$

Table III shows the corresponding sums and integrals for both S_{11} and H_{11} and the ratio $\bar{\epsilon}_1$. The sums agree with the corresponding integrals to within 1.0%. The energy values are much better and agree to within 0.2%.

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Relativistic Corrections in Many-Electron Systems*

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I. INTRODUCTION

In almost every application of quantum mechanical methods to the description of many-electron systems, it has been assumed that a nonrelativistic treatment should give results accurate enough. This assumption is very seldom checked, and in the few cases where an approximate relativistic calculation has been carried out, the results indicate that for many systems the preceding assumption is not justified. In the present paper the interest is focused on the shifts in the total energies caused by relativistic effects, and because almost nothing is known so far about these shifts in molecular systems, results are given only for atomic systems. The limited material presented here does not imply that the theory of relativity has been completely forgotten in quantum chemistry. In fact, a great deal of work has been performed in studying the effect of spin-orbit interaction in atomic and molecular spectra and relativistic effects have also been considered in the theories of the Auger spectra[1] and of the cohesive energies of alkali metals,[2] to mention a few examples. But because the concept of the total energy of a system plays such a dominating role in the formulation of quantum mechanics, in particular in constructing the wave equation determining the wave function, the influence of the theory of relativity on the total energy is of special importance. This is even more obvious from the fact that the only possible way at present to calculate an energy difference, e.g., dissociation energies and spectra, is to calculate the total energies for the two states involved and then take the difference.

As an introductory and illustrative example of cases where relativistic effects are of importance, we may consider a hydrogenlike system with nuclear charge Z. In the ground state of this system the electron has, according to the Schrödinger theory, a root-mean-square velocity of the order of $2.2\times Z\times 10^8$ cm/sec, which means that even for fairly small Z the velocity of the electron is comparable to the velocity of light. By using classical arguments for $Z=92$, one should expect a relativistic correction of about 50% of the nonrelativistic energy. In the relativistic quantum mechanics as developed by Dirac, the correction predicted in this case is around 15%. The structure of the Dirac theory is in many respects different from the nonrelativistic Schrödinger theory. The main differences are that the wave function for one electron has four components which are determined from first-order equations and that the spin of the electron from the beginning is built into the theory and not added as an extra postulate as in the Schrödinger theory. This inclusion of spin leads to relativistic terms which have no counterpart in classical relativistic mechanics. Apart from some small

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[1] W. N. Asaad, Proc. Roy. Soc. (London) **A249**, 555 (1959).

[2] J. Callaway, R. D. Woods, and V. Sirounian, Phys. Rev. **107**, 934 (1957).

discrepancies of a quantum electrodynamical origin, the Dirac theory is able to explain many experimental facts concerning one-electron systems. One is therefore inclined to believe that the Dirac theory is a good starting point for a relativistic quantum mechanical treatment of many-electron systems. It has been found, however, that whereas the Schrödinger theory can be extended to more than one electron as, e.g., the extensive work on the helium atom indicates,[3,4] considerable difficulties are involved in the generalization of the Dirac theory to many-electron systems and today a basic theory for such systems does not exist. In the past, two different approaches based on the Dirac theory have been made to an approximate relativistic treatment of many-electron systems. Breit[5] extended the Dirac theory to two electrons but he was forced to introduce some approximations in the electron-electron interaction term and the resulting theory is not fully Lorentz invariant. The other approach has the character of a practical calculating scheme. It extends the Hartree and Hartree-Fock approximations to include relativistic effects by using the Dirac Hamiltonian instead of the nonrelativistic Schrödinger one-electron operator. Some results obtained from these two approximations are given in the following two sections.

II. RELATIVISTIC SCF THEORY

The Hartree and, in particular, the Hartree-Fock approximations[6] have had a considerable success in giving fair quantitative results for atomic systems. These approximations assume that the total wave function can be written either as a product or as an antisymmetrized product of one-electron functions, respectively. When trial functions of this form are used in the variation principle, the equations determining the one-electron functions are a set of coupled nonlinear equations because of the electron-electron interaction. An essential feature of these two approximations is the independent-particle character, which makes it possible to generalize the one-electron part of the Hamiltonian to include relativistic effects by using the Dirac theory. This generalization supplemented with the assumption that the electrons interact only nonrelativistically has been used by Swirles[7] in deriving relativistic SCF equations. Because 4-component one-electron functions have to be used, the formalism is slightly changed as compared with the conventional SCF theory. Equations (1) give an example of the type of equations the two radial parts P and Q in the 4-component wave function satisfy in the Hartree approximation:

TABLE I. Orbital energies from nonrelativistic and relativistic Hartree calculations and corresponding experimental quantity. In Rydberg units. The results are taken from reference 9 (Cu^+) and 11 (Hg).

		Cu^+ $Z=29$			Hg $Z=80$	
Level	NR	Rel	Exptl.	NR	Rel	Exptl.
$1s$	658	664.8	661.4	5553	6145.7	6115.9
$2s$	78.45	79.52	80.8	925	1081.8	1093.3
$2p_{\frac{1}{2}}$		70.66	70.2		1041.7	1046.9
	69.86	*1.52*	*1.5*	892	*143.8*	*141.9*
$2p_{\frac{3}{2}}$		69.14	68.7		897.9	905.0
$3s$	8.97	8.98	9.1	216.9	255.7	262.5
$3p_{\frac{1}{2}}$		6.01			236.1	241.7
	6.08	*0.19*		200.6	*31.4*	*31.9*
$3p_{\frac{3}{2}}$		5.82			204.7	209.8
$3d_{\frac{3}{2}}$		1.02			173.2	176.0
	1.12	*0.02*		170.5	*6.8*	*6.7*
$3d_{5/2}$		1.00			166.4	169.3

$$\left.\begin{aligned}(dP/dr)+(k/r)P+[\alpha(V(r)-\epsilon)+2\alpha^{-1}]Q&=0\\(dQ/dr)-(k/r)Q-\alpha[V(r)-\epsilon]P&=0\\k=-(l+1)\quad&\text{for } j=l+\tfrac{1}{2}\\=+l\quad&\text{for } j=l-\tfrac{1}{2}.\end{aligned}\right\}\quad(1)$$

In atomic units[8] the velocity of light is α^{-1} where α is the fine structure constant. ϵ is the orbital energy and $V(r)$ is the potential energy of the electron. If exchange effects are included (Hartree-Fock approximation), the last terms in Eq. (1) are replaced by a sum of terms involving the Q's and P's describing the other electrons.[7]

Relativistic Hartree calculations have been carried out for Cu^+ by Williams,[9] Hg and Hg^{2+} by Mayers,[10] and Hg, U, Pt, W, Fe by Cohen.[11] All these calculations give orbital energies which for the inner shells agree with observed x-ray levels to within 1%. Table I gives some of the results for Hg and Cu^+ together with the nonrelativistic Hartree results and the corresponding observed quantity. The calculations on Hg by Mayers and Cohen do not agree completely. In general the Mayers' calculation gives slightly larger orbital energies, but the difference does not affect the general implications of the calculations. The results given in Table I show that, at least for high nuclear charges where the relativistic effects are of special importance, the major part of the difference between the nonrelativistic and experimental results is explained. The influence of, e.g., exchange effects and relativistic terms in the electron-electron interaction is not known, but they most probably do not change the situation drastically.

The relativistic SCF results also can be used to illustrate another consequence of the inclusion of relativistic terms in the Hamiltonian. In Fig. 1 a comparison is made between the relativistic and non-

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[3] T. Kinoshita, Phys. Rev. **105**, 1490 (1957); Phys. Rev. **115**, 336 (1959).

[4] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958); Phys. Rev. **115**, 1216 (1959).

[5] H. A. Bethe and E. E. Salpeter, *Handbuch der Physik* (Springer-Verlag, Berlin, 1957), Vol. 35. (This paper contains a detailed discussion of the Dirac theory and the Breit approximation with references to the original papers.)

[6] D. R. Hartree, Repts. Progr. Phys. **11**, 113 (1948); *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).

[7] B. Swirles, Proc. Roy. Soc. (London) **A152**, 625 (1935). (Some corrections to this paper are given in reference 6, p. 143.)

[8] The atomic unit (a.u.) is defined by $\hbar=e=m=1$. 1 a.u. $=2\ \mathrm{Ry}_\infty=219\,474.6\ \mathrm{cm}^{-1}=27.2097$ ev $=627.7$ kcal/mole.

[9] A. O. Williams, Phys. Rev. **58**, 723 (1940).

[10] D. F. Mayers, Proc. Roy. Soc. (London) **A241**, 93 (1957).

[11] S. Cohen, University of California Radiation Laboratory Repts. 8389, 8633–35, 8734 (unpublished).

relativistic total radial charge density for Hg^{2+}. A quantity Δ defined by

$$\Delta=\int_0^r (\rho_{\mathrm{R}}-\rho_{\mathrm{NR}})dr$$

is plotted as function of r. ρ_{R} and ρ_{NR} are the total relativistic and nonrelativistic radial charge densities. Δ may be interpreted as the increase of charge in a sphere of radius r round the nucleus caused by the relativistic treatment. The letters K, L, $\cdots$ in the figure give the positions of the K, L shell . . . in the relativistic calculation, and the numbers below the letters give the total charge in the spheres with the radii determined by these positions. Figure 1 clearly demonstrates that there is a considerable contraction of the electronic charge cloud. Because the relativistic treatment shifts the positions of the shells with respect to the nonrelativistic ones, maxima and minima occur in $\Delta(r)$.

III. PERTURBATION TREATMENT BASED ON THE BREIT THEORY

In the relativistic SCF approximation discussed in Sec. II, the basic assumption is that the interaction between the electrons can be approximately described by the electrostatic Coulomb potential. A more complete relativistic treatment of the interaction is exceedingly difficult to give and up till now, only approximations have been discussed. Most well known of these is the Breit treatment[5] which handles the relativistic part of the electron-electron interaction by perturbation theory. In practical applications one uses approximate solutions of the Schrödinger equation and makes a first-order perturbation calculation taking into account terms of order α^2 (Pauli approximation). The operators we have to consider in this case have been given by Hirschfelder et al.[12] for a molecular system. Here we confine our interest to a two-electron atom without external fields, in which case the relativistic part of the Breit Hamiltonian in the Pauli approximation is

$$\left.\begin{aligned}
&H_{\mathrm{rel}}=\alpha^2(H_1+H_2+H_3+H_4+H_5),\\
&H_1=-\tfrac{1}{8}(p_1{}^4+p_2{}^4),\\
&H_2=-\tfrac{1}{2}(1/r_{12})\{\mathbf{p}_1\cdot\mathbf{p}_2+[\mathbf{r}_{12}\cdot(\mathbf{r}_{12}\cdot\mathbf{p}_1)\mathbf{p}_2]/r_{12}{}^2\},\\
&H_3=\tfrac{1}{2}\{[\mathbf{E}_1\times\mathbf{p}_1+(2/r_{12}{}^3)\mathbf{r}_{12}\times\mathbf{p}_2]\cdot\mathbf{s}_1\\
&\qquad\qquad+[\mathbf{E}_2\times\mathbf{p}_2+(2/r_{12}{}^3)\mathbf{r}_{12}\times\mathbf{p}_1]\cdot\mathbf{s}_2\},\\
&H_4=i/4(\mathbf{p}_1\cdot\mathbf{E}_1+\mathbf{p}_2\cdot\mathbf{E}_2),\\
&H_5=-(8\pi/3)(\mathbf{s}_1\cdot\mathbf{s}_2)\delta^{(3)}(\mathbf{r}_{12})\\
&\qquad\qquad+\frac{1}{r_{12}{}^3}\left[\mathbf{s}_1\cdot\mathbf{s}_2-\frac{3(\mathbf{s}_1\cdot\mathbf{r}_{12})(\mathbf{s}_2\cdot\mathbf{r}_{12})}{r_{12}{}^2}\right]',\\
&\mathbf{E}_i=-\nabla_i[(Z/r_1)+(Z/r_2)-(1/r_{12})].
\end{aligned}\right\}\quad(2)$$

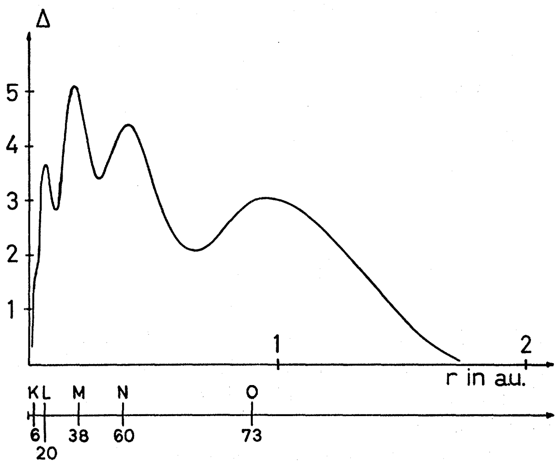

FIG. 1. The difference Δ between the relativistic and nonrelativistic total radial charge density for Hg^{2+} based on the Mayers' calculation.[10] Δ in electronic charges.

TABLE II. Comparison of the relativistic corrections for H-like systems obtained using α^2 approximation and Dirac theory. In atomic units. $\Delta E=E_{\mathrm{rel}}(\alpha^2)-E_{\mathrm{rel}}$ (Dirac).

Z	$U-Z$	$E_{\mathrm{rel}}(\alpha^2)$	ΔE
6	0.012	−0.009	0.000
10	0.053	−0.067	0.000
16	0.218	−0.438	0.002
20	0.426	−1.071	0.006
25	0.833	−2.622	0.023
30	1.439	−5.455	0.069
35	2.284	−9.994	0.175

For a detailed discussion of (2) we refer to reference 5. The physical interpretation of the operators in (2) is: H_1 gives the variation of mass with velocity, H_2 represents the magnetic orbit-orbit interaction, H_3 is the well-known spin-orbit interaction, H_4 is a term characteristic for the Dirac theory[13] and has no obvious physical interpretation, and H_5 is the spin-spin interaction. The validity of the α^2 approximation can easily be checked by considering a hydrogenlike system. Boys and Price[14] have used a trial function of the form $\psi=U^{\frac{3}{2}}\pi^{-\frac{1}{2}}\exp(-Ur)$ and minimized the energy with respect to U including relativistic terms of order α^2 in the Hamiltonian. In Table II the results obtained are compared with the energies given by the complete Dirac expression. We notice that $U>Z$, which means that there is a contraction of the electronic charge cloud, an effect which we also noted in the relativistic SCF treatment (Fig. 1). From Table II it is also obvious that if we are interested in results having chemical accuracy, where the total energy should be correct to about 10^{-3} a.u.$\approx$0.6 kcal/mole, then the α^2 approximation cannot be used for systems equivalent to a hydrogenlike one with $Z>15$. Table II also shows that the relativistic corrections increase rapidly with in-

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[12] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 1045.

[13] This term gives rise to Dirac δ-function terms.

[14] S. F. Boys and V. E. Price, Phil. Trans. Roy. Soc. (London) **A246**, 451 (1954).

TABLE III. Comparison of some expectation values (in a.u.) calculated from different variational wave functions for He (after Bethe-Salpeter[5]).

Wave function	H-like	Hartree	Hylleraas 3 term	6 term	18 term	Pekeris[a]
$-E_{\mathrm{NR}}$	2.8438	2.8670	2.9024	2.9032	2.9037	2.9037
$\langle\delta(\mathbf{r}_1)\rangle$	1.530	1.798	1.798	1.817	1.8102	1.8104
$\langle\delta(\mathbf{r}_{12})\rangle$	0.191	0.188	0.116	0.111	0.1072	0.1064
$\langle p^4\rangle$	40.54	52.46	53.42	54.50	54.072	54.088
Σ	+0.078	−1.227	−1.694	−1.860	−1.807	−1.813

[a] See reference 4.

creasing Z. In the α^2 approximation the leading term is Z^4. For $Z=30$ the nonrelativistic energy is $\frac{1}{2}\times 30^2=450$ a.u. and hence the relativistic correction is larger than 1% of that.

As already mentioned, the Breit theory is, in general, used for perturbation calculations of the relativistic corrections. It is of interest to know how the results depend on the choice of the unperturbed functions. Table III gives the results for He based on various functions obtained by variation calculations of the nonrelativistic energy. Included in the table are also the nonrelativistic energy E_{NR} and a quantity Σ defined by

$$\Sigma=\langle H_1+H_4+H_5\rangle.$$

This quantity is proportional to the relativistic correction with the H_2 term in Eq. (2) omitted. $\langle H_2\rangle$ is zero for any wave function of orbital form. As one would expect, $\langle\delta(\mathbf{r}_{12})\rangle$ changes considerably when the correlated motion of the electrons is taken into account more completely, and, in order to get stabilized expectation values, rather complicated variational wave functions have to be used. The hydrogenlike functions actually give the wrong sign for the relativistic corrections.

Table IV summarizes the results calculated for He-like systems by Pekeris[4] and for a Ne-like system calculated by Fröman.[15] The latter calculation uses the Hartree-Fock functions as a basis for the perturbation treatment and, judging from the result in Table III, this should probably not give reliable results but, as discussed in reference 15, the outcome seems still to be fairly accurate. From Table IV we see that the dominating terms are $\langle H_1\rangle$ and $\langle H_4\rangle$ and because these terms have opposite signs, omission of the Dirac term $\langle H_4\rangle$ should lead to completely wrong results. The situation is somewhat similar to the nonrelativistic theory where there is a balance between the positive kinetic energy and the negative potential energy. For the He-like series the results obtained by Pekeris[4] can be condensed in the formula

$$-4\alpha^{-2}E_{\mathrm{rel}}\approx Z^4-1.7Z^3+2.2Z^2+\cdots.$$

The square of the nonrelativistic energy for this isoelectronic series gives

$$(E_{\mathrm{NR}})^2=Z^4-1.25Z^3+0.71Z^2+\cdots,$$

and comparing the two last expressions we are led to a very rough way of estimating the relativistic corrections, namely, to put them proportional to the square of the nonrelativistic energy. By using this type of estimate one may try to predict the relativistic correction for the hydrogen molecule. For the united atom (a ^{2}He atom) the relativistic correction is 22.78 cm^{-1} which gives 2.71 cm^{-1} as the correction for two infinitely separated hydrogen atoms compared with the correct value 2.92 cm^{-1} calculated from the Dirac theory. For H_2 at equilibrium internuclear distance one obtains 9.7 cm^{-1}, which means that one should expect the relativistic correction to the dissociation energy (38 288 cm^{-1}) to be around 7 cm^{-1}.

TABLE IV. Contributions from the different operators in (2) for the He-like systems (reference 4) and Al^{3+} (reference 15) in a.u.

System	$\langle H_1\rangle$	$\langle H_4\rangle$	$\langle H_5\rangle$	$\langle H_2\rangle$	$\alpha^{-2}E_{\mathrm{rel}}$
He	−13.52	11.38	0.33	−0.14	−1.95
C^{4+}	−14 15.8	1158.2	19.3	−2.3	−240.6
Ne^{8+}	−11 524.7	9350.1	102.5	−7.0	−2079.1
Al^{3+}	−36 230	28 320	240	···	−7670

Table V gives the total energy and the estimated relativistic corrections for some atomic systems. A comparison between the systems Al^{3+} and Al^{11+} again emphasizes that the major part of the relativistic corrections is found in the inner shells.

IV. DISCUSSION

The magnitude of the relativistic corrections, as given in the tables in this paper, all indicate that in general one cannot neglect them. Because of the Z^4 dependence (in the α^2 approximation), this is true for atomic systems with high nuclear charge and hence also for molecules and solids built from such atoms. Fortunately, most of the molecules of interest in quantum chemistry, e.g., organic molecules are composed of atoms having small nuclear charges, and if one wants to estimate the relativistic effects an approximate treatment would be sufficient. But when we compare the results of calculations with experimental measurements, which nowadays especially in spectroscopy are very accurate, even for these small nuclear-charge

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[15] A. Fröman, Phys. Rev. **112**, 807 (1958).

TABLE V. Total energies (E) and relativistic corrections (E_{rel}) in ev for some atomic systems.

System	He^+	He	C^{5+}	C^{4+}	Be	Al^{11+}	Al^{3+}	F^-
$-E$	54.4145	78.9997	489.95	882.02	399.2	4389.8	6552.5	2719.4
$-E_{\text{rel}}$	0.0029	0.0028	0.23	0.35	0.06	9	11	2.6

systems a careful analysis of relativistic effects may be necessary.

For high nuclear-charge systems our incomplete knowledge of the relativistic effects for many-electron systems strongly limits the accuracy of the results of *a priori* calculations. The development of a consistent theory for such systems should be of great interest to quantum chemists.

It is of some interest to compare the relativistic corrections with some nonrelativistic quantities. In the nonrelativistic quantum mechanical treatment of atoms and molecules, the interelectronic repulsion term in the Hamiltonian causes the major difficulty when solving the Schrödinger equation. The Hartree-Fock treatment approximates this interaction by introducing average fields and, as a consequence, the HF energy is not the exact energy. The deviation is called the correlation energy. Comparing the relativistic correction and the correlation energy we find that for the He-like systems the relativistic correction is energywise more important than the correlation energy if the nuclear charge is larger than ≈ 8. The corresponding nuclear charge for the Ne-like systems is 13. By comparing the *total* Coulomb repulsion energy of the electrons with the relativistic correction, we find that the latter is more important if the nuclear charge is larger than 40 (He-like systems) and 65 (Ne-like systems). These figures are rather discouraging if one considers the large effort spent in handling the correlation problem, but the results given in this paper makes it possible to justify to a certain extent the neglect of relativistic effects. These are mostly "localized" to the inner shells of the atoms, whereas this is most probably not true for the correlation energy, and consequently we have a good chance of an almost exact cancellation of the relativistic corrections .when we calculate an energy difference, provided that the inner shells are not changed. However, the relativistic effects are so large in most atoms that even a small change in the shells caused, e.g., by polarization may be of importance.