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Construction of the Foldy–Wouthuysen transformation and solution of the Dirac equation using large components only

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It is shown that it is possible to construct, within the framework of a basis set expansion method, the full Foldy–Wouthuysen transformation (i.e., to all orders in the inverse velocity of light) for an arbitrary potential once the Dirac equation has been solved. On this basis an iterative procedure to solve the Dirac equation is suggested that involves only the large component, obviating the time-consuming (at least in molecular calculations) introduction of large basis sets for a proper description of just the small components. The methods are used to compare the expectation value of the radial distance operator in the Dirac picture and in the Schrödinger picture for the orbitals of the Uranium atom. © 1996 American Institute of Physics. [S0021-9606(96)01930-7]

I. INTRODUCTION

As is well known,¹ the nonrelativistic limit of the Dirac equation for an electron in an external potential is not reached simply by letting the velocity of light go to infinity. Rather this limiting process entails a unitary transformation at the same time, which block diagonalizes the Dirac Hamiltonian by separating the positive and negative energy part of its spectrum. This unitary transformation, known as the Foldy–Wouthuysen transformation, is equivalent to a change of picture and consequently in comparing relativistic and nonrelativistic expectation values (other than the energy) one has to be aware that the same operator (such as the radial distance operator r in an atom) does not represent the same physical quantity in both pictures.^{1–4} Unfortunately this transformation is only known exactly *a priori* for a free particle. When an external potential is present, the transformation is usually determined by expanding in the inverse velocity of light to some finite order. In case the potential is Coulombic in nature, however, this expansion is known to be highly problematic, leading to divergencies except in the lowest order. This does not mean that the transformation as such does not exist, only that it should not be expanded in this way. In this paper we will show that it is quite possible to obtain this nonexpanded unitary transformation within the framework of a basis set method without resorting to any perturbational expansion once the Dirac equation has been solved for its positive energy solutions.

In Sec. III it is shown how on the basis of this method, one can in fact obtain the large components of the Dirac orbitals, and the energies, in a finite basis set approximation in an iterative way, without first solving the Dirac equation itself. This iterative procedure, which can also be used in self-consistent-field calculations, represents an alternative way to solve the Dirac equation that does not involve the small component. It is very clear that considerable advances have been made towards four-component methods for molecular calculations.^{5–7} Nevertheless, the need to describe the small components accurately, requiring fairly large numbers of basis functions, makes four-component molecular relativistic

calculations much more time consuming than the non-relativistic analogs. It is therefore still considered very worthwhile to explore schemes that obviate the explicit construction of the small components.^{8,9}

The methods are used to compare the expectation value of the radial distance operator in the Dirac picture and in the Schrödinger picture for the orbitals of the Uranium atom.

II. CONSTRUCTION OF THE FOLDY–WOUTHUYSEN TRANSFORMATION

The time-independent Dirac equation for an electron in an external potential V reads (in atomic units):

$$H^D \Psi_i^D \equiv \begin{pmatrix} V & c \vec{\sigma} \cdot \vec{p} \\ c \vec{\sigma} \cdot \vec{p} & V - 2c^2 \end{pmatrix} \begin{pmatrix} \phi_i^D \\ \chi_i^D \end{pmatrix} = E_i^D \begin{pmatrix} \phi_i^D \\ \chi_i^D \end{pmatrix} = E_i^D \Psi_i^D. \quad (1)$$

Here Ψ^D is the four-component Dirac wave function and ϕ^D and χ^D are its large and small components. The Dirac equation has positive and negative total energy solutions, while we are usually only interested in the positive energy part of the spectrum that describes electrons (rather than positrons). (The E_i^D have been shifted downward by mc^2 .) The nonexpanded Foldy–Wouthuysen transformation¹ decouples this four-component equation in two two-component equations, one of which has only positive energy eigenvalues and the other only negative ones. This transformation can be obtained in a rather simple form¹⁰ by using a unitary matrix U :

$$U = \begin{pmatrix} \frac{1}{\sqrt{1+X^\dagger X}} & \frac{1}{\sqrt{1+X^\dagger X}} X^\dagger \\ -\frac{1}{\sqrt{1+XX^\dagger}} X & \frac{1}{\sqrt{1+XX^\dagger}} \end{pmatrix} \quad (2)$$

to transform the Dirac–Hamiltonian H_D . The transformed Hamiltonian:

$$H = U H_D U^{-1} \quad (3)$$

is block-diagonal provided X satisfies:

$$-XV - Xc\vec{\sigma} \cdot \vec{p}X + c\vec{\sigma} \cdot \vec{p} + (V - 2c^2)X = 0. \quad (4)$$

The Foldy–Wouthuysen Hamiltonian H^{FW} is then given by

$$H^{\text{FW}} = \frac{1}{\sqrt{1+X^\dagger X}} (c\vec{\sigma} \cdot \vec{p}X + X^\dagger c\vec{\sigma} \cdot \vec{p} - 2c^2X^\dagger X + V + X^\dagger VX) \frac{1}{\sqrt{1+X^\dagger X}}, \quad (5)$$

while the relation between the four-component Dirac wave function Ψ^{D} and the two-component Foldy–Wouthuysen transformed wave function Ψ^{FW} reads:

$$\Psi_i^{\text{D}} = \begin{pmatrix} \phi_i^{\text{D}} \\ \chi_i^{\text{D}} \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{1+X^\dagger X}} \Psi_i^{\text{FW}} \\ X \frac{1}{\sqrt{1+X^\dagger X}} \Psi_i^{\text{FW}} \end{pmatrix}; \quad (6)$$

$$\Psi_i^{\text{FW}} = \sqrt{1+X^\dagger X} \phi_i^{\text{D}}.$$

From Eq. (6) it immediately follows that the two-component operator X has the special property that when working on the large component ϕ^{D} of the Dirac wave function it gives the small component¹⁰ χ^{D} , thus

$$X\phi_i^{\text{D}} = \frac{c}{2c^2 + E_i - V} \vec{\sigma} \cdot \vec{p} \phi_i^{\text{D}} = \chi_i^{\text{D}}. \quad (7)$$

This property we can use to calculate the eigenfunctions of the (Hermitian) non-negative operator $X^\dagger X$. Suppose we have solved the Dirac equation for a given external potential V . We can then assume that the large components of the normalized Dirac wave functions which have positive total energy eigenvalues are linearly independent (but not orthogonal) and form a complete basis for the two-component space. In this basis we can easily calculate matrix elements of the operator $X^\dagger X$:

$$\begin{aligned} \langle \phi_i^{\text{D}} | X^\dagger X | \phi_j^{\text{D}} \rangle &= \langle \phi_i^{\text{D}} | \vec{\sigma} \cdot \vec{p} \frac{c^2}{(2c^2 + E_i - V)(2c^2 + E_j - V)} \vec{\sigma} \cdot \vec{p} | \phi_j^{\text{D}} \rangle \\ &= \langle \chi_i^{\text{D}} | \chi_j^{\text{D}} \rangle = \delta_{ij} - \langle \phi_i^{\text{D}} | \phi_j^{\text{D}} \rangle, \end{aligned} \quad (8)$$

where the last equation follows from the fact that the Dirac wave functions are orthonormal. If we diagonalize the resultant matrix we will find the eigenfunctions θ_i and eigenvalues λ_i^θ of the operator $X^\dagger X$ in this basis. We are then able to express the orthogonal eigenfunctions θ_i in terms of Dirac large components ϕ_j^{D} and vice versa:

$$\theta_i = \sum_j c_{ij}^{\theta\phi} \phi_j^{\text{D}}; \quad \phi_i^{\text{D}} = \sum_j c_{ij}^{\phi\theta} \theta_j. \quad (9)$$

Consequently we can use Eq. (6) to write the Foldy–Wouthuysen transformed wave function Ψ^{FW} as

$$\Psi_i^{\text{FW}} = \sum_{j,k} \sqrt{1 + \lambda_j^\theta} c_{ij}^{\phi\theta} c_{jk}^{\theta\phi} \phi_k^{\text{D}}. \quad (10)$$

We therefore have an explicit expression for the Foldy–Wouthuysen transformed wave functions that only involves the eigenvalues and eigenfunctions of essentially the overlap matrix of the large components of the Dirac solutions. This transformed wave function can subsequently be used to calculate various properties in the transformed picture (see Sec. IV). Of course, in practice finite basis sets will have to be used, with a concomitant loss of accuracy.

Some insight into the nature of the operator $X^\dagger X$ can be obtained by examining its classical form:

$$X^\dagger X = \frac{p^2 c^2}{(2c^2 + E - V)^2} = \frac{p^2 c^2}{(\sqrt{c^4 + p^2 c^2 + c^2})^2}. \quad (11)$$

Clearly for small momenta it will approximately be equal to $p^2/4c^2$, while for high momenta it will approach 1. Consequently for a free particle, this operator has a continuous spectrum between zero and one, while its eigenfunctions in this case will be plane waves.

III. ITERATIVE SOLUTION

We can use the ideas of the last section to formulate an iterative procedure to solve the Dirac equation in an external potential V that avoids using the small component entirely. Using Eqs. (5) and (6) we can write the Foldy–Wouthuysen transformed Dirac equation

$$H^{\text{FW}} \Psi_i^{\text{FW}} = E_i \Psi_i^{\text{FW}} \quad (12)$$

as an equation for the large component ϕ^{D} of the Dirac wave function, by multiplying it by $\tilde{S}^{1/2}$:

$$\tilde{H} \phi_i^{\text{D}} = E_i \tilde{S} \phi_i^{\text{D}}, \quad (13)$$

where

$$\tilde{H} = c\vec{\sigma} \cdot \vec{p}X + X^\dagger c\vec{\sigma} \cdot \vec{p} - 2c^2X^\dagger X + V + X^\dagger VX, \quad (14)$$

$$\tilde{S} = 1 + X^\dagger X. \quad (15)$$

Equation (13) is now in the standard form of an eigenvalue equation with a metric \tilde{S} . In the basis set of large components we can determine the matrix elements of the operators \tilde{H} and \tilde{S} , with the help of Eq. (7).

Equation (13) can be solved in an iterative manner. Suppose we have an estimate for the large components and the orbital energies, which will be called ϕ_i^0 and E_i^0 respectively, where i runs over the different approximate (positive energy) solutions of the Dirac equation (the number of which will be equal to the size of the large component basis set) and the superscript will indicate the number of the cycle in the subsequent iterative procedure. We then proceed from the $N-1$ th cycle to N th cycle in the following way.

We will first normalize every ϕ_i^{N-1} such that the orbital density is normalized to 1:

$$\langle \phi_i^{N-1} | \phi_i^{N-1} \rangle + \langle \phi_i^{N-1} | \vec{\sigma} \cdot \vec{p} \frac{c^2}{(2c^2 + E_i^{N-1} - V)^2} \vec{\sigma} \cdot \vec{p} | \phi_i^{N-1} \rangle = 1. \quad (16)$$

The matrix elements of the operator \tilde{S} are then approximated in the basis of large components ϕ_i^{N-1} according to Eq. (7) as

$$\begin{aligned} \langle \phi_i^{N-1} | \tilde{S} | \phi_j^{N-1} \rangle &= \langle \phi_i^{N-1} | 1 + X^\dagger X | \phi_j^{N-1} \rangle \\ &= \langle \phi_i^{N-1} | 1 + \vec{\sigma} \cdot \vec{p} \\ &\quad \times \frac{c^2}{(2c^2 + E_i^{N-1} - V)(2c^2 + E_j^{N-1} - V)} \\ &\quad \times \vec{\sigma} \cdot \vec{p} | \phi_j^{N-1} \rangle, \end{aligned} \quad (17)$$

while the matrix elements of the Hamiltonian \tilde{H} are determined from:

$$\begin{aligned} \langle \phi_i^{N-1} | \tilde{H} | \phi_j^{N-1} \rangle &= \langle \phi_i^{N-1} | V + \vec{\sigma} \cdot \vec{p} \frac{c^2}{(2c^2 + E_i^{N-1} - V)} \vec{\sigma} \cdot \vec{p} + \vec{\sigma} \cdot \vec{p} \frac{c^2}{(2c^2 + E_j^{N-1} - V)} \vec{\sigma} \cdot \vec{p} \\ &\quad - \vec{\sigma} \cdot \vec{p} \frac{c^2(2c^2 - V)}{(2c^2 + E_i^{N-1} - V)(2c^2 + E_j^{N-1} - V)} \vec{\sigma} \cdot \vec{p} | \phi_j^{N-1} \rangle \\ &= \langle \phi_i^{N-1} | V + \vec{\sigma} \cdot \vec{p} \frac{c^2}{(2c^2 - V)} \vec{\sigma} \cdot \vec{p} | \phi_j^{N-1} \rangle \\ &\quad - \langle \phi_i^{N-1} | \vec{\sigma} \cdot \vec{p} \frac{E_i^{N-1} E_j^{N-1} c^2}{(2c^2 + E_i^{N-1} - V)(2c^2 + E_j^{N-1} - V)(2c^2 - V)} \vec{\sigma} \cdot \vec{p} | \phi_j^{N-1} \rangle. \end{aligned} \quad (18)$$

The first term can be recognized as the zeroth order regular approximation (ZORA) to the Dirac Hamiltonian extensively discussed in earlier papers.¹¹⁻¹³ The ZORA approach was shown to already give quite accurate approximations to the full Dirac energies in many cases. The last term, which corrects this ZORA Hamiltonian, is small if the orbital energies involved are small compared to c^2 .

Diagonalizing the generalized eigenfunction equation, one obtains improved eigenvalues E_i^N and eigenfunctions ϕ_i^N . By iterating to self-consistency we obtain solutions to the Dirac equation without ever having to calculate the small component explicitly. The price to be paid is that the equation has to be solved iteratively. On the other hand this price is not as large as it may seem if one considers the usual case that the potential is not fixed but is also determined iteratively until self-consistency is reached. In particular in the density functional method the improved potential can be determined from the improved density at the end of each iterative cycle described above and one can converge both the self-consistent-field potential and the Dirac large component at the same time. This way of iteratively solving for the Dirac orbital energies and large components therefore is similar to the iterative SCF procedure followed in Dirac-Fock methods anyway, but it has to be noted that the matrix elements of \tilde{H} have to be calculated in a basis set that changes from cycle to cycle. The method is nevertheless interesting, and may well be competitive, since it avoids the large bases needed to describe the small components accurately. Note also that the matrix to be constructed and diagonalized has only roughly half of the size of the full Dirac

Hamiltonian matrix, being limited to the positive energy space.

A very good starting point for the iterative procedure is formed by the zeroth order ZORA equation which we studied before¹¹ and which appears explicitly as the first term in Eq. (18). We know from the results of Ref. 12, that the ZORA Hamiltonian is bounded from below. Since the second term in Eq. (18) is small if the orbital energies are small compared to c^2 , we expect that this term does not destroy the boundedness from below. This expectation is borne out by the results to be presented in Sec. IV. We note however that it is crucial to start with ‘‘positive’’ total energies $E_i > -c^2$. When starting with positron-like energies $E_i < -2c^2$, one may end up with converged positron-like solutions of the Dirac equation, because the iterative procedure is also valid for those states. We find in Sec. IV that we always converge to positive total energies, when we start with positive total energies and with an initial wave function (the ZORA wave function) that is already quite accurate. It is clear that the present method may be used if it is felt desirable, after obtaining the ZORA solutions, to improve the results to the level of full Dirac solutions. In view of the accuracy of the ZORA solutions for the valence electrons,¹¹ this will hardly ever be the case for problems of chemical bonding, but it may be useful for (deep) core levels.

IV. NUMERICAL TEST RESULTS

It is obvious that the method discussed in the previous section will be most useful for molecules, since in molecular calculations the small components lead to very large, often

TABLE I. Uranium 91+ orbital expectation values in a.u.

Orbital	$\langle r \rangle$	$\langle R \rangle - \langle r \rangle$ exact	$\langle R \rangle - \langle r \rangle$ first order	Orbital	$\langle r \rangle$	$\langle R \rangle - \langle r \rangle$ exact	$\langle R \rangle - \langle r \rangle$ first order
$1s_{1/2}$	0.01349	-0.00097	-0.00122	$5s_{1/2}$	0.3702	-0.00005	-0.00005
$2s_{1/2}$	0.05334	-0.00032	-0.00031	$5p_{1/2}$	0.3593	0.00005	0.00005
$2p_{1/2}$	0.04247	0.00033	0.00031	$5p_{3/2}$	0.3819	-0.00010	-0.00010
$2p_{3/2}$	0.05183	-0.00058	-0.00061	$5d_{3/2}$	0.3602	0.00010	0.00010
$3s_{1/2}$	0.1263	-0.00014	0.00014	$5d_{5/2}$	0.3668	-0.00015	-0.00015
$3p_{1/2}$	0.1154	0.00015	0.00014	$5f_{5/2}$	0.3342	0.00015	0.00015
$3p_{3/2}$	0.1289	-0.00027	-0.00027	$5f_{7/2}$	0.3376	-0.00020	-0.00020
$3d_{3/2}$	0.1072	0.00028	0.00027	$6s_{1/2}$	0.5411	-0.00004	-0.00003
$3d_{5/2}$	0.1116	-0.00040	-0.00041	$6p_{1/2}$	0.5302	0.00004	0.00003
$4s_{1/2}$	0.2319	-0.00008	-0.00008	$6p_{3/2}$	0.5574	-0.00007	-0.00007
$4p_{1/2}$	0.2211	0.00008	0.00008	$6d_{3/2}$	0.5357	0.00007	0.00007
$4p_{3/2}$	0.2390	-0.00015	-0.00015	$6d_{5/2}$	0.5435	-0.00010	-0.00010
$4d_{3/2}$	0.2173	0.00016	0.00015	$7s_{1/2}$	0.7446	-0.00003	-0.00002
$4d_{5/2}$	0.2228	-0.00023	-0.00023				
$4f_{5/2}$	0.1902	0.00023	0.00023				
$4f_{7/2}$	0.1932	-0.00030	-0.00031				

prohibitive, computation times. In the present paper we restrict ourselves to a test calculation on the uranium ion with only one electron, where we can compare with exact results, and to the neutral uranium atom where we can test the self-consistent procedure within the density functional framework (here we used the simple $X\alpha$ potential). Having established the viability of the proposed method, we will in the present paper use the fact that we achieve the construction of the Foldy–Wouthuysen transformation. This makes it possible to address the issue of the effect of the Dirac to Foldy–Wouthuysen picture change on expectation values for the operator \mathbf{r} .

As a basis set for the calculation of the neutral atom we used the Dirac type Slater orbitals (DTOs) with fractional exponents we discussed in an earlier paper⁸ and which were shown to give accurate representations of the large components of the Dirac orbitals in this case. In the hydrogenic case (U^{91+}), the exact solutions of the large components of the Dirac orbitals are a combination of a finite number of DTOs, for the calculated orbitals. These DTOs were added with some extra DTOs in our basis set, to get sufficient flexibility to also represent accurately the Foldy–Wouthuysen transformed orbitals, which resemble the renormalized large components. In both the ion and the neutral atom the method described above quickly converged and the orbital energies of the full Dirac calculations were reproduced to high numerical accuracy, only limited by the fact that we use numerical integration for the calculation of matrix elements. The fact that we obtain the Dirac result to any desired precision testifies to the correctness of our procedure.

An interesting question that can now be answered, concerns the difference between the two distinct observables that are represented by the operator \mathbf{r} in the Dirac picture and in the Schrödinger (Foldy–Wouthuysen) picture respectively. In an earlier paper⁴ we studied this question using the Foldy–Wouthuysen transformation to first order only, but now we are in a position to investigate the influence of

higher orders on this picture change. The expectation value of the “Dirac position” is given by

$$\langle r \rangle = \langle \Psi^D | \vec{r} | \Psi^D \rangle = \langle \Psi^{FW} | U^{FW} \vec{r} (U^{FW})^\dagger | \Psi^{FW} \rangle, \quad (19)$$

while on the other hand the expectation value of the “Schrödinger position” reads:

$$\langle R \rangle = \langle \Psi^{FW} | \vec{r} | \Psi^{FW} \rangle = \langle \Psi^D | (U^{FW})^\dagger \vec{r} U^{FW} | \Psi^D \rangle. \quad (20)$$

In Table I we show differences between these two observables for some orbitals of the hydrogen-like Uranium 91+ ion. The expectation value of the Dirac position can be calculated analytically¹⁴:

$$\langle r \rangle = \frac{(\gamma + n - |\kappa|)(3N^2 - \kappa^2) - \kappa N}{2ZN}, \quad (21)$$

with

$$\gamma = \sqrt{\kappa^2 - \frac{Z^2}{c^2}}; \quad N = \sqrt{(n - |\kappa| + \gamma)^2 + \frac{Z^2}{c^2}}. \quad (22)$$

In first order⁴ the difference between the Schrödinger and Dirac position for a hydrogenic orbital with quantum number n and κ is given by:

$$\langle R \rangle - \langle r \rangle = \frac{Z\kappa}{4c^2 n^2}, \quad (23)$$

where Z is the nuclear charges. The table shows that the influence of higher order terms in the Foldy–Wouthuysen transformation is generally quite small, except in the case of the $1s_{1/2}$ orbital where more than 25% of the effect is seen to arise from these higher order contributions. As an example of the self-consistent method we solved the equations for a neutral Uranium atom using the simple $X\alpha$ version of the density functional method. The same DTO basis set was used as in Ref. 8, where the Dirac equation was solved using a basis set for the large component only. The results are in perfect agreement with each other. In Table II we again com-

TABLE II. Neutral uranium orbital expectation values in a.u.

Orbital	$\langle r \rangle$	$\langle R \rangle - \langle r \rangle$	Orbital	$\langle r \rangle$	$\langle R \rangle - \langle r \rangle$
$1s_{1/2}$	0.01364	-0.00095	$5s_{1/2}$	0.6668	-0.000027
$2s_{1/2}$	0.05650	-0.00030	$5p_{1/2}$	0.6938	0.000025
$2p_{1/2}$	0.04576	0.00032	$5p_{3/2}$	0.7735	-0.000046
$2p_{3/2}$	0.05599	-0.00054	$5d_{3/2}$	0.8673	0.000040
$3s_{1/2}$	0.1471	-0.00012	$5d_{5/2}$	0.8957	-0.000059
$3p_{1/2}$	0.1382	0.00012	$5f_{5/2}$	1.487	0.000038
$3p_{3/2}$	0.1566	-0.00022	$5f_{7/2}$	1.550	-0.000046
$3d_{3/2}$	0.1350	0.00023	$6s_{1/2}$	1.473	-0.000011
$3d_{5/2}$	0.1405	-0.00033	$6p_{1/2}$	1.650	0.000011
$4s_{1/2}$	0.3199	-0.00006	$6p_{3/2}$	1.897	-0.000018
$4p_{1/2}$	0.3182	0.00006	$6d_{3/2}$	3.237	0.000011
$4p_{3/2}$	0.3549	-0.00010	$6d_{5/2}$	3.499	-0.000015
$4d_{3/2}$	0.3515	0.00010	$7s_{1/2}$	4.118	-0.000004
$4d_{5/2}$	0.3625	-0.00014			
$4f_{5/2}$	0.3517	0.00014			
$4f_{7/2}$	0.3571	-0.00017			

pare the difference of the two position observables. Although the basis set results for the valence orbitals of the neutral Uranium atom have an accuracy of about 0.1% for the expectation value of r , the picture change effects are expected in absolute value to be more accurate, because the same basis set was used for both orbitals. For the deep core the picture change effects are roughly the same as for the hydrogenic Uranium. For valence orbitals the absolute value in the picture change is about 4 to 7 times smaller than in the hydrogenic case, which is much smaller than the accuracy of the used basis set. Also in the neutral atom there is opposite behavior for $\kappa < 0$ orbitals and $\kappa > 0$ orbitals.

V. CONCLUSIONS

In this paper the nonexpanded Foldy–Wouthuysen transformation is constructed for an arbitrary potential. On the basis of this construction an iterative procedure is formulated that constitutes an alternative way for solving the Dirac equation, obviating the need for a small component basis. The procedure seems especially attractive when used in a self-consistent-field scheme, since then the iterative procedure can be run concurrently with the SCF iterations. The method has been applied to the calculation of the picture change effects in the expectation value of the position opera-

tors with the uranium atom as an example. Higher than first order effects of this picture change turn out to be only important for the deep core orbitals, where they can be as large as 25% in the case of hydrogen-like uranium.

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