PHYSICAL REVIEW A VOLUME 44, NUMBER 3 1 AUGUST 1991

Finite-volume variational method for the Dirac equation

Peter Hamacher and Jürgen Hinze
Fakultät für Chemie, Universität Bielefeld, D-4800 Bielefeld, Germany

(Received 10 December 1990; revised manuscript received 4 March 1991)

A finite-volume variational principle based on the Dirac Hamiltonian is formulated in a way similar to the Kohn variational principle for the logarithmic derivative used in nonrelativistic electron-atom scattering. As in R-matrix methods, the essential idea is to solve the Dirac equation variationally within a finite reaction volume for a given total energy of the system. In contrast to previous methods, we do not need to impose any unphysical boundary conditions on the trial function. The continuation of the variational solution into the outer region is represented by a standard close-coupling expansion. The K matrix is obtained by matching the variational solutions with the solutions in the outer region on the surface enclosing the reaction volume.

I. INTRODUCTION

As in all R-matrix treatments, the total system, target plus electron, is treated only within a finite reaction volume. In the outer region the scattering wave function is represented by the usual close-coupling expansion. The scattering information is obtained by matching the inner and outer solutions at the boundary. The traditional nonrelativistic R-matrix theory of Wigner and Eisenbud [1] was developed into an effective method for the calculation of atomic and molecular collision processes [2,3]. In this method a complete set of discrete eigenstates of the Hamiltonian, describing all the particles, are calculated by imposing as boundary condition on the wave function a fixed value for the logarithmic derivative normal on the reaction surface; however, these restrictions are artificial and unphysical.

An alternative nonrelativistic version, the R-matrix eigenvalue method [4] based on the Kohn variational principle [5], provides an effective means for the determination of optimal electronic wave functions for the description of electron scattering processes for any fixed (low) energy. In this version, the trial function is not required to satisfy any specified boundary condition on the reaction surface. Rather the logarithmic normal derivatives are obtained as eigenvalues for any fixed total energy. The use of the R-matrix eigenvalue method within the framework of nonrelativistic configuration mixing calculations is widespread and yields excellent results [6–8]. For atoms and ions with atomic numbers larger than $\simeq 20$, relativistic effects in the scattering process become more and more important. It is therefore desirable to have a theory which starts with the Dirac Hamiltonian instead of using merely relativistic corrections (spin-orbit interactions, spin-other-orbit terms, etc.) to the nonrelativistic formulation [9,10].

An R-matrix procedure for electron-atom scattering using the Dirac Hamiltonian was formulated by Chang [11] and applied [12] in a manner analogous to the Wigner-Eisenbud method. The method of Chang and also the traditional theory can be understood as an application of the Ritz principle restricted to the finite reaction volume. To achieve Hermiticity of the Dirac Hamiltonian within this volume, Chang imposes artificial fixed boundary conditions to the variational wave function, i.e., all continuum orbitals included in the calculation must be constrained to have the same ratio of the large and small components at the boundary. Applying the Ritz variational principle then yields a set of *discrete* energy eigenvalues and eigenstates defined in the interior of the reaction volume. The total scattering wave function for any energy is expanded in terms of the variational solutions, where the expansion coefficients are determined by continuity requirements of the inner and outer wave functions at the boundary.

As has been pointed out [13,14] the fixed boundary condition basis expansion of the Wigner-Eisenbud treatment is not uniformly convergent, while the absence of fixed boundary conditions in the alternative R-matrix eigenvalue method provides greater flexibility. With this motivation we present on the basis of the Dirac Hamiltonian a relativistic version of this more flexible method. To this end we derive an alternative variational expression, where the total energy appears as a *given* parameter. In contrast to Chang's formulation, the continuum orbitals and thus the total trial function need not have any specified behavior at the reaction surface, allowing for greater freedom of the trial function. Further it is shown that the functions that give extremes are continuum solutions of the Dirac equation optimized for the energy desired. This is closer to the physical situation, where in the scattering process the energy is given by the energy of the initial channel plus the energy of the incident electron.

In Sec. II we will give a description of the finite volume variational principle. A comparison with the work of Chang is also presented. As described in Secs. III and IV, a generalized relativistic R matrix can be calculated in terms of the variational solutions. This R matrix connects the large and the small components of the close-coupling solution linearly at the boundary. It will be shown that, if terms of order $O(1/r)$ are neglected, the generalized R matrix becomes the familiar R matrix in the nonrelativistic limiting case. Finally the K matrix is obtained by matching the R matrix on the boundary.

II. THE VARIATIONAL PRINCIPLE

The total number of electrons for the scattering system is denoted by N, where the target atom consists of $N-1$ electrons, and the electronic spatial vectors and the spin coordinates are $\mathbf{r}_\mu$, $\mu=1,\dots,N$ and s_μ, $\mu=1,\dots,N$, respectively. With this any spatial configuration of the electrons in the $3N$-dimensional configuration space $\mathbb{R}^{3N}$ is represented by the $3N$-tuple $\mathbf{r}=\{\mathbf{r}_1,\dots,\mathbf{r}_N\}\in\mathbb{R}^{3N}$.

The essential idea in the R-matrix treatment for relativistic scattering systems is to solve the stationary multiparticle Dirac equation only within a reaction volume $\mathcal{V}$ enclosed by a hypersurface $\mathcal{S}$ in configuration space. For applications in electron-atom scattering, this situation may be visualized by a nucleus centered sphere in physical space. The radius ρ_0 of this sphere is chosen appropriately large, so that the charge density of the target states can be neglected on and outside the sphere surface. Thus only the scattering electron can escape beyond the radius ρ_0. In this case, exchange effects outside the sphere are negligibly small and the interaction between the scattering electron and the target can be treated as a single-particle problem. If the scattering electron is inside the sphere, the motion of all electrons is highly correlated; the many-body interactions are strong and require the full N-electron treatment. This implies the definition of the reaction volume $\mathcal{V}$ containing all configuration space points $\mathbf{r}$ at which all electrons are located within the sphere of radius ρ_0. Denoting the radial coordinate of the μth electron with r_μ, the reaction volume $\mathcal{V}$ is represented by the equation

$$\mathcal{V}=\{\mathbf{r},\ \max(r_1,\dots,r_N)\le\rho_0\}\ , \tag{1}$$

and the corresponding reaction surface enclosing the volume $\mathcal{V}$ is given by

$$\mathcal{S}=\{\mathbf{r},\ \max(r_1,\dots,r_N)=\rho_0\}\ . \tag{2}$$

It is emphasized, that the reaction volume $\mathcal{V}$ in the $3N$-dimensional space $\mathbb{R}^{3N}$ is different from the sphere with radius ρ_0 in physical space $\mathbb{R}^3$.

We are concerned with the Dirac Hamiltonian operator of the N-electron system,

$$H_D=\sum_{\mu=1}^{N} h_D(\mu)+V\ . \tag{3}$$

Here $h_D(\mu)$ is the one-electron operator acting on the μth electronic coordinate

$$h_D(\mu)=-ic\boldsymbol{\alpha}(\mu)\cdot\boldsymbol{\nabla}_\mu+\beta'(\mu)c^2-Z/r_\mu \tag{4}$$

with the familiar Dirac matrices $\beta'(\mu)$ and $\boldsymbol{\alpha}(\mu)=(\alpha_x(\mu),\alpha_y(\mu),\alpha_z(\mu))$. The components $\alpha_x(\mu)$, $\alpha_y(\mu)$, and $\alpha_z(\mu)$ are given to be

$$\alpha_x(\mu)=\begin{bmatrix}0 & \sigma_x(\mu)\\ \sigma_x(\mu) & 0\end{bmatrix},\quad \alpha_y(\mu)=\begin{bmatrix}0 & \sigma_y(\mu)\\ \sigma_y(\mu) & 0\end{bmatrix},\quad \alpha_z(\mu)=\begin{bmatrix}0 & \sigma_z(\mu)\\ \sigma_z(\mu) & 0\end{bmatrix}, \tag{5}$$

where $\sigma_x(\mu)$, $\sigma_y(\mu)$, and $\sigma_z(\mu)$ are the Pauli matrices acting on the μth spin variable. $\beta'(\mu)$ represents the matrix

$$\beta'(\mu)=\begin{bmatrix}0 & 0\\ 0 & -2\mathbf{1}_2\end{bmatrix}, \tag{6}$$

where $\mathbf{1}_2$ denotes the two-dimensional unit matrix. Finally

$$V=\sum_{\substack{\mu,\nu\\ \mu>\nu}}\frac{1}{|\mathbf{r}_\mu-\mathbf{r}_\nu|} \tag{7}$$

is the Coulomb interaction potential between the electrons thought to describe the dominant part of the electron-electron interaction. In the definitions above atomic units ($\hbar=e=m_e=1$) were used.

Similar to the nonrelativistic case the total wave function Ψ of the system, depending on all electronic spatial vectors and spin variables, is represented as a linear combination of configuration-state functions (CSF's),

$$\Psi=\sum_I \Phi_I C_I\ . \tag{8}$$

The Φ_I themselves are minimal superpositions of Slater determinants constructed out of four-component one-electron orbitals $\psi_{n_i\kappa_i m}$. For atomic scattering systems, these orbitals are chosen to be eigenfunctions of the operators $\mathbf{j}^2$, j_z, $\boldsymbol{l}^2$, and $\mathbf{s}^2$, where $\mathbf{j}=\boldsymbol{l}+\mathbf{s}$ is the sum of the one-electron angular momentum $\boldsymbol{l}$ and spin $\mathbf{s}$. Hence we can separate the radial part of $\psi_{n_i\kappa_i m}$,

$$\psi_{n_i\kappa_i m}(\mathbf{r}_\mu s_\mu)=\frac{1}{r}\begin{bmatrix}P_{n_i\kappa_i}(r_\mu)\chi_{\kappa_i m}(\omega_\mu s_\mu)\\ iQ_{n_i\kappa_i}(r_\mu)\chi_{-\kappa_i m}(\omega_\mu s_\mu)\end{bmatrix}, \tag{9}$$

where $\chi_{\kappa m}$ is a two-component spinor eigenfunction of the total angular momentum $\mathbf{j}$ belonging to the simultaneous eigenvalues κ of the operator $K=-1-\boldsymbol{\sigma}\cdot\boldsymbol{l}$. For reasons of simplicity we use the abbreviations $P_i=P_{n_i\kappa_i}$ and $Q_i=Q_{n_i\kappa_i}$ in the following discussion. One subset of the orbitals is defined to have zero amplitude at $r=\rho_0$ and another subset contains orbitals, which have nonvanishing amplitude for $r=\rho_0$ (open-type orbitals). In addition the orbitals and thus the shell functions are required to be orthonormal within the sphere of the radius ρ_0, i.e.,

$$\langle P_i|P_j\rangle+\langle Q_i|Q_j\rangle=\delta_{ij},\quad \kappa_i=\kappa_j\ , \tag{10}$$

where $\langle\ |\ \rangle$ indicates radial integration up to ρ_0. The CSF's are constructed in such a way, that all orbitals except at most one in each CSF must satisfy the boundary condition to be zero at $r=\rho_0$.

In the formulation of Chang [11], all open-type orbitals are constrained to have the same ratio of the small and large components at the boundary

$$\frac{Q_i(\rho_0)}{P_i(\rho_0)}=\beta=\text{const}\ , \tag{11}$$

where β is an arbitrarily given constant and i denotes an open-type shell. This boundary condition ensures hermiticity of the Dirac Hamiltonian within the finite reaction volume. Accordingly, the Ritz variational principle for the energy eigenvalues can be applied. The variational expression is

$$E=\frac{\langle\Psi|H_D|\Psi\rangle}{\langle\Psi|\Psi\rangle}\ , \tag{12}$$

where the scalar product $\langle\ |\ \rangle$ indicates summation over all spin variables s_μ and spatial integration of all electronic coordinates $\mathbf{r}_\mu$ within the finite reaction volume $\mathcal{V}$, i.e., radial integration of all radial coordinates up to the boundary ρ_0. Variation with respect to the coefficients C_I, i.e., diagonalizing the Dirac Hamiltonian matrix in the basis Φ_I, yields a set of *discrete* energy eigenvalues and eigenstates of the Dirac Hamiltonian defined in the interior of the reaction volume. Here, the total scattering wave function for any energy is expanded in terms of the energy eigenstates [see Eq. (14) of Ref. [11]], with expansion coefficients determined by the matching conditions of the inner and outer solutions at the boundary.

As outlined before, the Dirac Hamiltonian H_D is in general not Hermitian within the finite volume $\mathcal{V}$, but Hermiticity can be achieved by introducing restrictive conditions on the open type at $r=\rho_0$, as done by Chang [11]. In our formulation we need not impose any boundary conditions at $r=\rho_0$ on these orbitals and hence the basis functions Φ_I have no specified behavior on the reaction surface.

To this end we consider the extended Dirac Hamiltonian

$$\hat{H}_D=H_D+\Delta\ . \tag{13}$$

Here Δ is defined as a sum of one-electron operators each acting on the μth coordinate, i.e.,

$$\Delta=ic\sum_\mu \delta(r_\mu-\rho_0)\eta(\mu) \tag{14}$$

with the matrix $\eta(\mu)$ acting only on the small component

$$\eta(\mu)=\begin{bmatrix}0 & \sigma_r(\mu)\\ 0 & 0\end{bmatrix}, \tag{15}$$

where

$$\sigma_r(\mu)=\boldsymbol{\sigma}(\mu)\cdot\mathbf{r}_\mu/r_\mu \tag{16}$$

is the radial component of $\boldsymbol{\sigma}(\mu)$. As shown in the Appendix, $\hat{H}_D$ defined above is Hermitian in general within the finite volume $\mathcal{V}$ without any restrictions on the wave function on the reaction surface. With this, the derivation of the variational principle discussed in this paper begins by rearranging the Ritz formula (12), which we write by adding and subtracting Δ,

$$\langle\Psi|H_D+\Delta-E|\Psi\rangle-\langle\Psi|\Delta|\Psi\rangle=0\ . \tag{17}$$

We now introduce the (still unknown) parameter b by the equation

$$(\Delta-bT)\Psi=0\ . \tag{18}$$

Here the operator T is given by

$$T=\tfrac{1}{2}\sum_\mu \delta(r_\mu-\rho_0)\tau(\mu) \tag{19}$$

with $\tau(\mu)$ acts only on the large component

$$\tau(\mu)=\begin{bmatrix}1_2 & 0\\ 0 & 0\end{bmatrix}. \tag{20}$$

Equation (18) has to be understood as a boundary condition for the desired solution on the reaction surface $\mathcal{S}$, where we concentrate on wave functions for which the parameter b is *constant* for all points on $\mathcal{S}$. Since b is not known in advance for any fixed energy E, the goal of the calculation is to find b. For the later discussion in Sec. IV it should be remarked, that Eq. (18) is equivalent with

$$\left[\left[ic\eta(N)-\frac{b}{2}\tau(N)\right]\Psi\right]_{r_N=\rho_0}=0\ , \tag{21}$$

where the remaining radial coordinates are constrained by $r_i<\rho_0$, $i=1,\dots,N-1$. This can be shown, if the antisymmetry property of Ψ is considered. But for formal reasons, we will use Eq. (18) henceforth in this section. It should also be noted that (18) or (21) follows from the boundary condition (11) if $\beta=b/2c$; however, we do not need to impose this boundary condition onto the trial function, rather the variational principle yields it for the solution function.

Applying definition (18) and using the condition that b is constant over the reaction surface $\mathcal{S}$ we obtain from Eq. (17),

$$\langle\Psi|H_D+\Delta-E|\Psi\rangle-b\langle\Psi|T|\Psi\rangle=0\ . \tag{22}$$

Solving this for b yields the functional form

$$b[\Psi]=\frac{\langle\Psi|H_D+\Delta-E|\Psi\rangle}{\langle\Psi|T|\Psi\rangle}, \tag{23}$$

which is now defined for any *arbitrary* trial function, i.e., also for functions Ψ not solving the Dirac equation and not having the property (18). Note here, that the total energy E appears as a fixed but arbitrary parameter in the expression above. With the Hermiticity of the operators $H_D+\Delta$ and T (see the Appendix) the functional expression for b is obviously real. The variation of $b[\Psi]$ yields

$$\delta b[\Psi]=\frac{\langle\delta\Psi|H_D+\Delta-E-bT|\Psi\rangle+\text{c.c.}}{\langle\Psi|T|\Psi\rangle}\ , \tag{24}$$

where the abbreviation c.c. denotes the conjugate of the explicit term in the numerator. From this identity we can see the following. If Ψ extremalizes the variational expression (23), i.e., $\delta b[\Psi]=0$, then Ψ is a solution of the eigenvalue equation

$$(H_D+\Delta-E)\Psi=bT\psi \ , \tag{25}$$

where b appears as an eigenvalue and T plays the role of a metric. For $r_i<\rho_0 \ \forall i$ the surface terms $\Delta\Psi$ and $T\Psi$ do not contribute and the eigenequation above reads as the Dirac equation

$$(H_D-E)\Psi=0 \ . \tag{26}$$

For reasons of continuity, this equation is also satisfied on the boundary, so that the boundary condition $(\Delta-bT)\Psi=0$ additionally follows from the eigenequation (25). On the other side, if Ψ satisfies Eqs. (26) and (18), Ψ makes the variational expression $b[\Psi]$ stationary [see Eq. (24)]. These two statements, which form the finite volume variational principle for continuum solutions of the Dirac equation, can be summarized in the following way:

$$\delta b=0 \Longleftrightarrow \begin{cases}(H_D-E)\Psi=0, & \mathbf{r}\in\mathcal{V}\\ (\Delta-bT)\Psi=0. & \end{cases} \tag{27}$$

We see that the variational principle (27) can be understood as a method for solving the time independent Dirac equation in the continuum. Accordingly the solutions are determined by the stationary condition $\delta b[\Psi]=0$ for any given energy E within the reaction volume $\mathcal{V}$. It should be emphasized, that *no constraint* needs to be imposed on the trial function in showing $\delta b=0$.

In multichannel scattering problems having several degenerate continuum solutions, the discussion above is meant to hold for each independent variational solution Ψ_K and the corresponding boundary parameter b_K. Inserting the expansion (8) for the wave function into the variational expression (23) and defining the expansion coefficients C_{IK} for state K, the stationary condition $\partial b_K/\partial C_{IK}=0$ leads to the set of algebraic eigenequations

$$\sum_J(\hat{H}_{DIJ}-\delta_{IJ}E)C_{JK}=\sum_J T_{IJ}C_{JK}b_K \tag{28}$$

with the Hermitian matrix elements

$$\hat{H}_{DIJ}=\langle\Phi_I|\hat{H}_D|\Phi_J\rangle \tag{29}$$

and

$$T_{IJ}=\langle\Phi_I|T|\Phi_J\rangle \ . \tag{30}$$

The desired boundary parameters b_K and the expansion coefficients C_{IK} are obtained as the eigenvalues and eigenvectors of the eigenvalue problem (28), respectively. From here it is clear, that the variational principle can also be used for the determination of optimal orbitals including the unbound scattering orbitals in self-consistent-field (SCF) (Hartree-Fock) or even multiconfiguration-self-consistent orbital (MCSCO) sense [15]. To avoid the "variational collapse" [16, 17], which may arise in relativistic calculations, one has to use the same precaution as are necessary in relativistic bound-state calculations [17]. Experience has shown, that the problem of variational collapse is much more critical in calculations, where basis functions are used to represent the orbitals. For atoms, finite difference methods have been used effectively, and these calculations are not plagued by the collapse phenomenon.

III. SOLUTION IN THE OUTER REGION

Each individual target state considered in the scattering calculation is designed by $\Psi_{\Gamma\bar{J}\bar{M}}$, where $\bar{J}$ and $\bar{M}$ are the quantum numbers of the total target angular momentum and its projection onto the z axis, respectively. All other quantum numbers characterizing the target state are represented by Γ. With this we construct the channel functions for the large and small components by coupling the target atom states with the spin-angular function of the scattered electron to form eigenstates of $\mathbf{J}^2, J_z$ with the quantum numbers J,M for the total angular momentum of the system,

$$\Theta_\gamma=\sum_{m,\bar{M}}\Psi_{\Gamma\bar{J}\bar{M}}(1,\ldots,N-1)\begin{bmatrix}\chi_{\kappa m}(N)\\ 0\end{bmatrix}\langle\bar{J}\,\bar{M}\,j\,m|J\,M\rangle \ , \tag{31}$$

$$\bar{\Theta}_\gamma=\sum_{m,\bar{M}}\Psi_{\Gamma\bar{J}\bar{M}}(1,\ldots,N-1)\begin{bmatrix}0\\ \chi_{-\kappa m}(N)\end{bmatrix}\langle\bar{J}\,\bar{M}\,j\,m|J\,M\rangle \ , \tag{32}$$

where the composite index $\gamma=(\Gamma\bar{J}j)$ defines a scattering channel. Using the general property [18]

$$\sigma_r\chi_{\kappa m}=-\chi_{-\kappa m} \tag{33}$$

and the definitions (15) and (20), it can be shown that the following relations are satisfied by the channel functions:

$$\begin{aligned}&\eta(N)\bar{\Theta}_\gamma=-\Theta_\gamma, \quad \eta(N)\Theta_\gamma=0 \ ,\\ &\tau(N)\bar{\Theta}_\gamma=0, \quad \tau(N)\Theta_\gamma=\Theta_\gamma \ .\end{aligned} \tag{34}$$

The solutions of the Dirac equation in the outer region, i.e., when the radial coordinate r_N of the scattering electron exceeds the boundary ρ_0, are usually expanded in the following way:

$$\Psi_\gamma=\sum_{\gamma'=1}^{M} r_N^{-1}(\Theta_{\gamma'}y_{\gamma'\gamma}+i\bar{\Theta}_{\gamma'}z_{\gamma'\gamma}),\quad r_N\geq\rho_0\ , \tag{35}$$

where M is the number of open and closed channels and the functions $y_{\gamma'\gamma}$ and $z_{\gamma'\gamma}$ depending only on the radial coordinate r_N are the large and small components describing the radial motion of the scattered electron. There exist maximally M linearly independent solutions of the Dirac equation regular in the origin and having the form given in expansion (35), so $\gamma=1,\ldots,M$. Inserting the ansatz (35) into the Dirac equation and projecting onto the channel functions yields the set of $2M$ coupled first-order differential equations:

$$\begin{aligned}\frac{dy_{\gamma\gamma'}}{dr_N}+\frac{\kappa_\gamma}{r_N}y_{\gamma\gamma'}-\frac{1}{c}\left[2c^2+\varepsilon_\gamma+\frac{Z}{r_N}\right]z_{\gamma\gamma'}&=-\frac{1}{c}\sum_{\gamma''=1}^{M}\bar{V}_{\gamma\gamma''}z_{\gamma''\gamma'}\ ,\\ \frac{dz_{\gamma\gamma'}}{dr_N}-\frac{\kappa_\gamma}{r_N}z_{\gamma\gamma'}+\frac{1}{c}\left[\varepsilon_\gamma+\frac{Z}{r_N}\right]y_{\gamma\gamma'}&=\frac{1}{c}\sum_{\gamma''=1}^{M}V_{\gamma\gamma''}y_{\gamma''\gamma'}\ ,\end{aligned} \tag{36}$$

where ε_γ is the kinetic energy of the electron in channel γ and

$$V_{\gamma\gamma'}=\langle\Theta_\gamma|V|\Theta_{\gamma'}\rangle$$

and

$$\bar{V}_{\gamma\gamma'}=\langle\bar{\Theta}_\gamma|V|\bar{\Theta}_{\gamma'}\rangle$$

are the local coupling potentials depending only on r_N. By definition, the R matrix in relativistic scattering connects the solutions for the large and small components at ρ_0 in the following way:

$$y_{\gamma\gamma'}(\rho_0)=2c\sum_{\gamma''}R_{\gamma\gamma''}z_{\gamma''\gamma'}(\rho_0)\ . \tag{37}$$

To make the meaning of the relativistic R matrix introduced above more clear, we formally solve for the small component in the first part of Eq. (36), i.e.,

$$z_{\gamma\gamma'}=\sum_{\bar{\gamma}'}A^{-1}_{\gamma\bar{\gamma}}\left[\frac{dy_{\bar{\gamma}\gamma'}}{dr_N}+\kappa_{\bar{\gamma}}r_N^{-1}y_{\bar{\gamma}\gamma'}\right] \tag{38}$$

with

$$A_{\gamma\gamma'}=\frac{1}{c}\left[2c^2+\varepsilon_\gamma+\frac{Z}{r_N}\right]\delta_{\gamma\gamma'}-\frac{1}{c}\bar{V}_{\gamma\gamma'}\ . \tag{39}$$

Inserting the formal solution (38) into the R-matrix relation (37) we obtain

$$y_{\gamma\gamma'}(\rho_0)=2c\sum_{\gamma'',\bar{\gamma}'}R_{\gamma\gamma''}A^{-1}_{\gamma''\bar{\gamma}}\times\left[\frac{dy_{\bar{\gamma}\gamma'}}{dr_N}(\rho_0)+\kappa_{\bar{\gamma}}\rho_0^{-1}y_{\bar{\gamma}\gamma'}(\rho_0)\right]\ . \tag{40}$$

Considering the property of the inverse of the matrix A,

$$A^{-1}_{\gamma\gamma'}=\frac{1}{2c}\delta_{\gamma\gamma'}+O\left[\frac{1}{c^3}\right]\ ,$$

and dropping all terms of order $O(1/c^2)$ Eq. (40) can be written as

$$y_{\gamma\gamma'}(\rho_0)=\sum_{\gamma''}R_{\gamma\gamma''}\left[\frac{dy_{\gamma''\gamma'}}{dr_N}(\rho_0)+\kappa_{\gamma''}\rho_0^{-1}y_{\gamma''\gamma'}(\rho_0)\right]\ . \tag{41}$$

Thus, up to the terms of order $O(1/\rho_0)$ this equation reduces to the definition for the familiar R matrix in the nonrelativistic limit. With the help of the R matrix, the scattering information can be obtained as outlined below. For low energy scattering and small residual charge, the system (36) can be approximated by substituting the formal solution (38) into the second part of (36) and neglecting all terms of order $O(1/c^2)$. This yields

$$\left[\frac{d^2}{dr_N^2}-\frac{\kappa_\gamma(\kappa_\gamma+1)}{r_N^2}+\frac{2Z}{r_N}+2\varepsilon_\gamma\right]y_{\gamma\gamma'}(r_N)=2\sum_{\gamma''}V_{\gamma\gamma''}(r_N)y_{\gamma''}(r_N)\ . \tag{42}$$

These equations are the same asymptotic radial equations as occur in the nonrelativistic theory. It should be emphasized, that in the inner region no such approximation was made and it is here, that the major relativistic effects are expected to arise. In view of this, a stationary computer package [19] can be used to solve (42). For reasons of consistency, the reactance matrix or K matrix, which contains the total scattering information, is obtained by matching the solutions using Eq. (41). The matching process is then very similar to that used in the nonrelativistic R-matrix method.

IV. CALCULATION OF THE R MATRIX

An explicit expression to calculate the R matrix can be derived in the following way. The continuation of the variational solutions Ψ_K discussed in Sec. II into the outer region, denoted by Ψ_K^{out}, is expanded as

$$\Psi_K^{\text{out}}=\sum_{\gamma=1}^{M}r_N^{-1}(\Theta_\gamma w_{\gamma K}+i\bar{\Theta}_\gamma v_{\gamma K}),\quad r_N\geq\rho_0 \tag{43}$$

where the functions $w_{\gamma K}$ and $v_{\gamma K}$ are the large and small components of the scattering electrons, respectively. They depend only on the radial coordinate r_N and are also solutions of (36). As noted before, there exist M linearly independent solutions of the Dirac equation, so $K=1,\ldots,M$. The continuity condition on the boundary reads

$$(\Psi_K^{\text{out}})_{r_N=\rho_0}=(\Psi_K)_{r_N=\rho_0}\ . \tag{44}$$

We now consider Eq. (21) satisfied by the variational solutions Ψ_K,

$$\left[\left[ic\eta(N)-\frac{b_K}{2}\tau(N)\right]\Psi_K\right]_{r_N=\rho_0}=0\ . \tag{45}$$

Because of the continuity condition (44) we can insert expansion (43) into the equation above. Using the relations (34) yields

$$\sum_{\gamma} \Theta_{\gamma} \left[v_{\gamma K}(\rho_0) - \frac{b_K}{2c} w_{\gamma K}(\rho_0) \right] = 0 \, , \tag{46}$$

where the projections of the variational solutions onto the channel functions at ρ_0 are

$$w_{\gamma K}(\rho_0) = \langle \Theta_{\gamma} | \Psi_K \rangle_{r_N = \rho_0} \, , \tag{47}$$

$$v_{\gamma_K}(\rho_0) = -\mathrm{i} \langle \bar{\Theta}_{\gamma} | \Psi_K \rangle_{r_N = \rho_0} \, . \tag{48}$$

After multiplying Eq. (46) with the complex conjugate of the channel functions Θ_{γ} and integrating over all target coordinates and spin-angular variables of the scattering electron, we obtain

$$v_{\gamma K}(\rho_0) - \frac{b_K}{2c} w_{\gamma K}(\rho_0) = 0 \, . \tag{49}$$

Using this result we write the R-matrix relation (37) as

$$w_{\gamma K}(\rho_0) = 2c \sum_{\gamma'} R_{\gamma\gamma'} v_{\gamma' K}(\rho_0) = \sum_{\gamma'} R_{\gamma\gamma'} w_{\gamma' K} b_K \, . \tag{50}$$

Solving for $R_{\gamma\gamma'}$ yields the explicit expression in terms of the known quantities $w_{\gamma K}(\rho_0)$ and b_K^{-1}

$$R_{\gamma\gamma'} = \sum_{K=1}^{M} w_{\gamma K} b_K^{-1} w_{K\gamma'}^{-1} \, . \tag{51}$$

This is the spectral representation of the relativistic R matrix, which has the same form as obtained in previous works [4,8,20].

ACKNOWLEDGMENTS

The authors acknowledge the support by the Deutsche Forschungsgemeinschaft via SFB 216 "Polarisation und Korrelation in atomaren Stosskomplexen."

APPENDIX

To show the Hermiticity of the extended Hamiltonian $\hat{H}$, Eq. (13), and the operator T, Eq. (19), with respect to the finite volume scalar product $\langle \mid \rangle$, it is sufficient to show the Hermiticity of the matrix elements in the basis of the CSF's Φ_I, Eqs. (29) and (30). The latter are expressed in terms of one- and two-electron integrals, i.e.,

$$\hat{H}_{DIJ} = \sum_{i,j} \hat{h}_{Dij} \gamma_{ij}^{IJ} + \sum_{i,j,k,l,\nu} (\langle P_i | U_{kl\nu} | P_j \rangle + \langle Q_i | U_{kl\nu} | Q_j \rangle) \Gamma_{ijkl\nu}^{IJ} \tag{A1}$$

and

$$T_{IJ} = \tfrac{1}{2} \sum_{i,j} \langle P_i | \delta(r - \rho_0) | P_j \rangle \gamma_{ij}^{IJ} \, , \tag{A2}$$

where the sums are performed over all shell indices. Here the angular brackets indicate integration of the radial coordinate up to the boundary ρ_0. The structure factors γ_{ij}^{IJ} and $\Gamma_{ijkl\nu}^{IJ}$, independent on the shell functions, are the reduced transition matrix elements of the first and second order between CSF's in the space spanned up by the shell functions, and they depend on the shell occupations, the symmetry coupling, and the reduction from orbitals to shell functions achieved by integration over spin and the angles. For the structure factors, the following symmetry properties can be shown:

$$\gamma_{ij}^{IJ} = \gamma_{ji}^{JI*} , \quad \Gamma_{ijkl\nu}^{IJ} = \Gamma_{jilk\nu}^{JI*} \, . \tag{A3}$$

The one-electron matrix elements are given by [21]

$$\hat{h}_{Dij} = \left\langle Q_i \left| c\frac{d}{dr} + \frac{c\kappa_i}{r} \right| P_j \right\rangle + \left\langle P_i \left| -c\frac{d}{dr} + \frac{c\kappa_i}{r} \right| Q_j \right\rangle + \langle P_i | c\delta(r - \rho_0) | Q_j \rangle + \left\langle P_i \left| -\frac{Z}{r} \right| P_j \right\rangle + \left\langle Q_i \left| -2c^2 - \frac{Z}{r} \right| Q_j \right\rangle ,$$

which is easily shown to be Hermitian by partial integration of the terms containing the first derivative d/dr,

$$\hat{h}_{Dij} = \hat{h}_{Dji}^{*} \, . \tag{A4}$$

Additionally, we can write

$$\langle P_i | \delta(r - \rho_0) | P_j \rangle = \langle P_j | \delta(r - \rho_0) | P_i \rangle^* \, , \tag{A5}$$

because of the Hermiticity of the Dirac δ function. The two-electron potentials in (A1) are given by [21]

$$U_{kl\nu}(r) = \left\langle P_k \left| \frac{r_<^{\nu}}{r_>^{\nu+1}} \right| P_l \right\rangle + \left\langle Q_k \left| \frac{r_<^{\nu}}{r_>^{\nu+1}} \right| Q_l \right\rangle \tag{A6}$$

satisfying

$$\langle P_i | U_{kl\nu} | P_j \rangle = \langle P_j | U_{lk\nu} | P_i \rangle^* \tag{A7}$$

and

$$\langle Q_i | U_{kl\nu} | Q_j \rangle = \langle Q_j | U_{lk\nu} | Q_i \rangle^* \, . \tag{A8}$$

Considering Eqs. (A3), (A4), (A5), (A7), and (A8) in the explicit expressions for the matrix elements $\hat{H}_{DIJ}$ and T_{IJ}, we obtain by renaming the summation indices

$$\begin{aligned}\hat{H}_{DIJ} &= \sum_{i,j} \hat{h}_{Dij}\gamma_{ij}^{IJ} + \sum_{i,j,k,l,\nu} (\langle P_i|U_{kl\nu}|P_j\rangle + \langle Q_i|U_{kl\nu}|Q_j\rangle)\Gamma_{ijkl\nu}^{IJ} \\ &= \sum_{i,j} \hat{h}_{Dji}\gamma_{ji}^{IJ} + \sum_{i,j,k,l,\nu} (\langle P_j|U_{lk\nu}|P_i\rangle + \langle Q_j|U_{lk\nu}|Q_i\rangle)\Gamma_{jilk\nu}^{IJ} \\ &= \sum_{i,j} \hat{h}^{*}_{Dij}\gamma_{ij}^{JI*} + \sum_{i,j,k,l,\nu} (\langle P_i|U_{kl\nu}|P_j\rangle^{*} + \langle Q_i|U_{kl\nu}|Q_j\rangle^{*})\Gamma_{ijkl\nu}^{JI*} \\ &= \hat{H}^{*}_{DJI}\end{aligned}$$

and

$$T_{IJ} = \tfrac{1}{2}\sum_{i,j} \langle P_i|\delta(r-\rho_0)||P_j\rangle\gamma_{ij}^{IJ} = \tfrac{1}{2}\sum_{i,j} \langle P_j|\delta(r-\rho_0)|P_i\rangle\gamma_{ji}^{IJ} = \tfrac{1}{2}\sum_{i,j} \langle P_i|\delta(r-\rho_0)|P_j\rangle^{*}\gamma_{ij}^{JI*} = T^{*}_{JI} \ .$$

Hence, the operators $\hat{H}$ and T are Hermitian in the space spanned by the basis functions Φ_I.

[1] E. P. Wigner and L. Eisenbud, Phys. Rev. **72**, 29 (1947).
[2] P. G. Burke and M. J. Seaton, Methods Comput. Phys. **10**, 1 (1971).
[3] P. G. Burke and W. D. Robb, Adv. At. Mol. Phys. **11**, 143 (1975).
[4] C. H. Greene, Phys. Rev. A **28**, 2209 (1983).
[5] W. Kohn, Phys. Rev. **74**, 1762 (1948).
[6] P. F. O'Mahony and C. H. Greene, Phys. Rev. A **31**, 250 (1985).
[7] C. H. Greene, Phys. Rev. A **36**, 2706 (1987).
[8] P. Hamacher and J. Hinze, J. Phys. B **22**, 3397 (1989).
[9] M. R. Scott and P. G. Burke, J. Phys. B **13**, 4299 (1980).
[10] M. R. Scott and A. J. Taylor, Comput. Phys. Commun. **25**, 347 (1982).
[11] J. J. Chang, J. Phys. B **8**, 2327 (1975).
[12] P. H. Norrington and I. P. Grant, J. Phys. B **14**, L261 (1981).
[13] R. K. Nesbet, *Variational Methods in Electron-Atom-Scattering-Theory* (Plenum, New York, 1980).
[14] C. H. Greene, in *Fundamental Processes of Atomic Dynamics*, edited by J. S. Briggs, K. Kleinpoppen, and H. O. Lutz (Plenum, New York, 1988).
[15] J. Hinze and P. Hamacher, J. Chem. Phys. **92**, 4372 (1990).
[16] W. H. E. Schwarz and H. Wallmeier, Mol. Phys. **46**, 1045 (1982).
[17] W. Kutzelnigg, Int. J. Quantum Chem. **25**, 107 (1984).
[18] A. Messiah, *Quantum Mechanics* (North-Holland/Plenum, New York, 1975), Vol. II.
[19] M. A. Crees, Comput. Phys. Commun. **19**, 103 (1980).
[20] P. Hamacher, Doctoral thesis, Universität Bielefeld, 1990.
[21] I. P. Grant, Adv. Phys. **19**, 747 (1970).