

Ab-initio nonrelativistic and relativistic Hartree-Fock calculations for both closed- and open-shell molecules using GTO basis

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Abstract. Computer programs for *ab-initio* Hartree-Fock and Dirac-Hartree-Fock calculations on closed- and open-shell atoms and molecules have been indigenously developed. Sample results of high quality are given for Li, Be, LiH and Be₂. As a byproduct of these calculations the importance of considering relativistic effects in the investigation of the elusive bound-state structure of Be₂ is clearly indicated.

Keywords. Hartree-Fock; Dirac-Hartree-Fock; ab-initio; program development.

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1. Introduction

This communication is to announce the indigenous development of computer programs for *ab-initio* nonrelativistic and relativistic Hartree-Fock calculations on molecules. Two sets of programs have been prepared, one set for nonrelativistic Hartree-Fock (HF) calculations and the other set for Dirac-Hartree-Fock (DHF) calculations. Options have been kept for both closed-shell and open-shell self-consistent-field treatments. These programs have been written for calculations with gaussian type orbitals (GTOs). These have been extensively tested for accuracy. Integrals of the nonrelativistic type have been calculated using the formulae derived by Taketa *et al* [1]. The programs for the DHF calculation were actually developed by us more than a decade back, but these could not be tried here owing to lack of adequate computing facilities. These were tested elsewhere [2]. We have now rewritten and adapted these programs for execution in CDC Cyber 180/840 mainframe computer presently available to us. The detailed description of the method of calculations, the structure of the programs belonging to the two sets and the choice of the relativistic basis spinors will be published as broad follow-up papers later.

2. Hamiltonian

The *N*-electron Hamiltonians used for the nonrelativistic and relativistic calculations are as follows. The nonrelativistic Hartree-Fock calculations are based on the nonrelativistic Hamiltonian

$$H_{\text{nonrel}} = \sum_{i=1}^N h(i) + \sum_{i<j} |r_i - r_j|^{-1} \quad (1)$$

where the one-electron Hamiltonian h is given by

$$h(i) = -2^{-1}\nabla_i^2 - \sum_n^{\text{nuclei}} Z_n |r_i - R_n|^{-1}. \quad (2)$$

The relativistic (Dirac-Hartree-Fock) calculations are based on the Dirac-Coulomb Hamiltonian

$$H_{\text{DC}} = \sum_{i=1}^N h_{\text{D}}(i) + \sum_{i < j} |r_i - r_j|^{-1} \quad (3)$$

where the one-electron Dirac Hamiltonian is given by

$$h_{\text{D}}(i) = c\alpha_i \cdot p_i + c^2\beta_i - 1_i \sum_n^{\text{nuclei}} Z_n |r_i - R_n|^{-1} \quad (4)$$

Atomic units have been used throughout. In the above r_i indicates the position vector of the i th electron and R_n the position vector of nucleus n .

The use of these Hamiltonian operators amounts to performing the Hartree-Fock calculations under two conventional approximations. These approximations are as follows. First, we ignore the effect of mass correction as discussed by Bethe and Salpeter [3]. Second, these calculations are done under the Born-Oppenheimer approximation. Therefore, the total energy will be calculated by adding V_{nn} to the computed total energy for electrons, where V_{nn} is the energy of nucleus-nucleus interaction,

$$V_{nn} = \sum_{m < n}^{\text{nuclei}} \sum_{m < n} Z_m Z_n |R_m - R_n|^{-1}. \quad (5)$$

The nonrelativistic Hartree-Fock equations and the Hartree-Fock-Roothaan equations for solving the self-consistent-field problem are common knowledge. The relativistic Hartree-Fock equations for a general molecule have been discussed by several authors including Malli and Oreg [4], Malli [5], Datta and Ewig [2] and Datta and Devaiah [6]. Due to paucity of space these equations are not described in this paper. Instead we give an account of the most important features of nonrelativistic and relativistic Hartree-Fock treatments in the following.

3. Special features

The relativistic calculations are associated with several theoretical and technical difficulties. The theoretical difficulties are referred to as variational collapse [7, 8] and continuum dissolution [9]. Physicists have suggested the use of positive-energy projected Hamiltonians for the Dirac-Hartree-Fock calculations [9, 10]. Mittleman [11] has shown that the Hartree-Fock reduction of H_{DC} results in the same orbital energies as the Hartree-Fock reduction of the appropriately projected Hamiltonian. Nevertheless, by considering a "maximization followed by minimization" procedure, the DHF equations can be derived without the use of projection operators and without any scruple [6]. The step of maximization leads to a trial function belonging to the "positive-energy subspace" (that is, this function corresponds to the N -electron sector of Fock space). In a basis set expansion procedure one may not *explicitly* carry

out the first step of maximization. In that case the possibility of variational collapse, or rather the possibility of getting a wrong estimate of the relativistic corrections, gives rise to a difficulty in the choice of a good basis set [7, 12]. This difficulty is a technical one. As stated earlier, the choice of relativistic basis sets will be described elsewhere. Another technical difficulty involves the excessive load on computation as the number of primitive functions required for a relativistic calculation should be four times the number of primitives needed for an equivalent nonrelativistic calculation.

The Breit operator embodies the most important effects of the interaction of the electron with a virtual (transverse) photon. The correction to total energy due to Breit interaction can be calculated with a minor modification of the present programs. The computations, however, will be expensive. This development will be reported elsewhere.

For the nonrelativistic treatment we have employed the usual LCAO-MO scheme. The LCAS-MS (linear combinations of atomic spinors as molecular spinors) scheme [2, 4] has been adopted in the relativistic work with the generalization that the 'atomic' spinors need to be four-component basis spinors with atomic angular momentum symmetries retained in each nonvanishing component of every spinor to expedite the computation. Thus one may even choose basis spinors with vanishing upper components or vanishing lower components. For the calculations reported here, however, we have employed basis spinors which look like relativistic atomic orbitals.

The open-shell calculations, both nonrelativistic and relativistic, are under the constraints that only one open shell for a given symmetry is allowed and that in the direct product of the additional irreducible species of more than one open shells, a given irreducible species does not occur more than once [5]. The speed of light has been taken to be 137.036 a.u. We present here the results of a few sample calculations carried out within the context of the procedure and limitations discussed above.

4. Results and discussion

Table 1 gives a summary of the function of all the programs developed indigenously as part of our laboratory programme on HF and DHF calculations. A detailed description will be published in the near future.

The atomic calculations (open-shell and closed-shell) have all been carried out with extensive basis sets. The results are always near the Hartree-Fock and Dirac-Fock limits. Calculations on LiH and Be₂ molecules (both closed-shell) have been performed with the minimal basis sets. The molecular calculations have been performed with atomic orbitals (spinors) of near Hartree-Fock (near Dirac-Fock) quality as basis functions. Therefore, the results obtained are in reality standards for minimal basis calculations.

For the nonrelativistic treatment we have selected the near Hartree-Fock quality GTO basis sets for lithium and beryllium (Li ²S 18s and Be ¹S 18s) where each basis function is expanded into a set of eighteen atom-centered gaussian functions [13]. For hydrogen the 10-gaussian expansion of O-Ohata *et al* [14] has been augmented by two more gaussians of exponents 10000.0 and 5000.0. The resulting 12-gaussian expansion gives a difference of 1.2×10^{-6} a.u. in the 1s orbital energy. Molecular calculations have been performed at the experimental bond length ($R = 3.015$ a.u.) for LiH and at two bond lengths, $R = 4.2$ a.u. (2.22 Å) and $R = 4.63$ a.u. (2.45 Å), for Be₂.

Table 1. Functions of the programs developed. The figure in parenthesis under the name of each program indicates the number of statements.

Program	Functions
Nonrelativistic Hartree-Fock calculation (program set: LCAOMO)	
NREL1E (1712)	Calculates nonrelativistic one-electron integrals: overlap integrals kinetic energy integrals electron-nuclear potential energy integrals r^n integrals for atoms ($n = -3, -2, -1, 1, 2, 3, 4, 6$)
NREL2E (1172)	Calculates nonrelativistic two-electron repulsion integrals over gaussians and over basis functions.
SCFCOS (1249)	Performs Hartree-Fock-Roothaan self-consistent-field calculation for both closed-shell and open-shell molecules. It also calculates $\langle r^n \rangle$ expectation values for each atomic orbital.
Relativistic Hartree-Fock calculation (program set: LCASMS)	
REL1E (3392)	Calculates relativistic one-electron integrals. Integrals over the nonrelativistic basis functions are calculated first. These involve overlap integrals, integrals of $\partial/\partial x$ etc., nuclear attraction integrals and for atoms, r^n integrals. Integrals over the basis spinors are then calculated.
REL2E (1702)	Calculates two-electron repulsion integrals over nonrelativistic basis functions and then calculates two-electron repulsion integrals over basis spinors.
RELCOS (1736)	Performs the self-consistent-field calculation for both closed-shell and open-shell molecules. It also calculates $\langle r^n \rangle$ expectation values for each atomic orbital.

The bond length 4.2 a.u. was chosen to compare our present result with the result calculated earlier [2]. The bond length 4.63 a.u. is the experimentally found equilibrium bond length of Be_2 in vapour phase [15].

The nonrelativistic total and orbital energies are given in table 2. The atomic results are only for the purpose of comparison. They agree very nicely with the near Hartree-Fock results calculated by Partridge [13]. In table 2 the molecular orbital energies are given to sixth decimal place and total energy to seventh decimal. A convergence factor of 10^{-9} for total energy has been used in these calculations. The total and orbital energies calculated for Be_2 with internuclear separation 4.2 a.u. represent an improvement over the results of our earlier calculation [2] that employed a 10-gaussian expansion for each basis function. The improvement is caused by the 18-gaussian expansion used in the present work, and it occurs at the fourth place after the decimal point in every energy value.

The form of the relativistic $s_{1/2}$ spinors is shown in table 3. The lower component functions have been generated by applying the operator $(2c)^{-1}\sigma.p$ on the upper component functions and then multiplying the results by a suitable factor (close to 1.0) so as to maintain the correct virial ratio (ratio of potential and kinetic energies).

Relativistic total and orbital energies are given in table 4. There is an excellent agreement between the computed total energies for atoms and the total energies calculated numerically by Desclaux [16]. The computed relativistic orbital energies, however, differ slightly (in the fifth significant digit) from the numerically calculated values. The reason for this difference is as follows. Since nonrelativistic basis functions have been used to form the two upper components, the charge density for each orbital

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Table 2. Computed nonrelativistic total and orbital energies in atomic units. Total energy is indicated by *E* and orbital energy is shown against the name of the orbital.

Species		Computed values (this work)	Literature value	Reference
H	<i>E</i>	-0.4999988	-0.500000	
Li	<i>E</i>	-7.4327266	-7.432727	Partridge
	1s	-2.4777400	-2.477741	[13]
	2s	-0.1963226	-0.196323	
Be	<i>E</i>	-14.5730223	-14.573023	Partridge
	1s	-4.7326690	-4.732669	[13]
	2s	-0.3092692	-0.309269	
LiH (<i>R</i> = 3.015 a.u.)	<i>E</i>	-7.9603942	-7.794720	Sundholm
	1σ	-2.468815		[17] ^a
	2σ	-0.294808		
Be ₂ (<i>R</i> = 4.2 a.u.)	<i>E</i>	-29.0750463	-29.0743	Datta and Ewig
	1σ _g	-4.750917	-4.7510	[2] ^b
	1σ _u	-4.750820	-4.7509	
	2σ _g	-0.405697	-0.4060	
	2σ _u	-0.251723	-0.2516	
Be ₂ (<i>R</i> = 4.63 a.u.)	<i>E</i>	-29.1003704		
	1σ _g	-4.739462		
	1σ _u	-4.739438		
	2σ _g	-0.387109		
	2σ _u	-0.258397		

^(a)Numerical Hartree-Fock-Slater calculation.

^(b)Each STO expanded in a set of ten GTO's.

Table 3. Form of relativistic $s_{1/2}$ basis spinors. The basis functions, s , p_x , p_y and p_z are not individually normalized. The basis spinors are normalized.

$m_j = 1/2$	$m_j = -1/2$
s	0
0	$-s$
$-i3^{-1/2}p_z$	$3^{-1/2}(p_y + ip_x)$
$3^{-1/2}(p_y - ip_x)$	$-i3^{-1/2}p_z$

is slightly less than the actual value near the nucleus. The charge density is again slightly less in the outermost region as the GTO's fall off faster than exponential functions. This is made clear by the expectation values $\langle r^n \rangle$ for atomic orbitals in table 5 where we find a slight decrease for $n = -2, -1$ and (sometimes for) 6 and a slight increase for $n = 1, 2$ and 4 from the numerically calculated values.

Relativistic total and orbital energies for LiH and Be₂ are given in table 6. Although we have carried out only a minimal basis calculation, the total energies calculated for LiH are seen to be consistently better than those obtained from two-dimensional

Table 4. Relativistic total and orbital energies (E_{rel} and ϵ) for atoms. Energy values are in atomic unit.

	Present work	Numerical calculation Desclaux [16]
Hydrogen	Virial ratio = -1.00000998	
E_{rel}	-0.500005465	-0.500006656 ^a
$E_{rel} - E_{nonrel}$	-0.000006655	-0.000006656 ^a
Lithium	Virial ratio = -1.00000006	
E_{rel}	-7.4335330	-7.43353
$E_{rel} - E_{nonrel}$	-0.0008064	-0.00080
$\epsilon_{1s_{1/2}}$	-2.478126	-2.477979
$\epsilon_{2s_{1/2}}$	-0.1963400	-0.1963389
Beryllium	Virial ratio = -1.00000032	
E_{rel}	-14.5758908	-14.57590
$E_{rel} - E_{nonrel}$	-0.0028684	-0.00288
$\epsilon_{1s_{1/2}}$	-4.734000	-4.733498
$\epsilon_{2s_{1/2}}$	-0.3093576	-0.3093221

^(a) Exact solutions.**Table 5.** Expectation values of r^n for the relativistic atomic orbitals. Numerically calculated values are also shown.

n		-2	-1	1	2	4	6
H	1s PW	1.9999	0.99999	1.5000	3.0000	22.501	315.17
	Num	2.0002	1.0000	1.5000	2.9999	22.499	314.98
Li	1s PW	14.889	2.6851	0.57311	0.44678	0.53216	1.2501
	Num	14.898	2.6856	0.57305	0.44670	0.53208	1.2472
	2s PW	0.43521	0.34537	3.8736	17.738	565.64	28883.00
	Num	0.43572	0.34544	3.8733	17.736	565.71	28949.00
Be	1s PW	27.752	3.6820	4.1498	0.23293	0.14201	0.16665
	Num	27.786	3.6833	4.1498	0.23286	0.14196	0.16655
	2s PW	1.0549	0.52246	2.6494	8.4263	135.17	3649.0
	Num	1.0571	0.52267	2.6489	8.4236	135.11	3649.6

PW: Present work.

Num: Numerical calculation [16].

fully numerical Hartree-Fock-Slater (HFS) and Dirac-Slater (DS) calculations [17]. The relativistic correction to total energy, defined as the difference between the calculated relativistic and nonrelativistic energies (E_{rel} and E_{nonrel}), more or less agrees with the correction calculated by the numerical method. For Be_2 ($R = 4.2$ a.u.) we find a relativistic correction to total energy that is about 20% smaller in absolute magnitude than the correction calculated earlier with a much smaller basis set.

The molecule Be_2 has proved to be very difficult to be described theoretically. The experimental dissociation energy is only 0.0036 a.u. [15]. Several configuration-interaction and other sophisticated nonrelativistic treatments involving static and dynamical correlation effects have been attempted, but it has been found that the shape of the calculated energy surface drastically changes from method to method

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Table 6. Relativistic total and orbital energies (E_{rel} and ϵ) for molecules in atomic unit.

	Present work	Literature value	Reference
LiH ($R = 3.015$ a.u.)			
E_{rel}	-7.9612147	-7.7955230	Sundholm
$E_{\text{rel}} - E_{\text{nonrel}}$	-0.0008205	-0.0008030	[17] ^a
$\epsilon_{1\sigma}$	-2.469200		
$\epsilon_{2\sigma}$	-0.294835		
Be ₂ ($R = 4.2$ a.u.)			
E_{rel}	-29.0808065	-29.0815	Datta and Ewig
$E_{\text{rel}} - E_{\text{nonrel}}$	-0.0057602	-0.0072	[2] ^b
$\epsilon_{1g1/2}$	-4.752247	-4.7523	
$\epsilon_{1u1/2}$	-4.752151	-4.7522	
$\epsilon_{2g1/2}$	-0.405788	-0.4064	
$\epsilon_{2u1/2}$	-0.251821	-0.2521	
Be ₂ ($R = 4.63$ a.u.)			
E_{rel}	-29.1061287		
$E_{\text{rel}} - E_{\text{nonrel}}$	-0.0057583		
$\epsilon_{1g1/2}$	-4.740792		
$\epsilon_{1u1/2}$	-4.740768		
$\epsilon_{2g1/2}$	-0.387195		
$\epsilon_{2u1/2}$	-0.258499		

(^a) Numerical Hartree-Fock-Slater and Dirac-Slater calculations.

(^b) Each basis function was expanded as a linear combination of ten gaussians. The Q -dependent two-electron integrals were not included in the calculation and a slightly different value of speed of light was used.

[18]. Our calculation shows that at the experimental equilibrium bond length ($R = 4.63$ a.u.) the relativistic correction to total energy is about -0.0058 a.u. (minimal basis results). The relativistic correction to binding energy is found to be $+2.145 \times 10^{-5}$ a.u. only. However, for the internuclear separation of 4.2 a.u. we find that the relativistic correction to the binding energy is -2.334×10^{-5} a.u. Thus in going from $R = 4.63$ a.u. to $R = 4.2$ a.u. relativistic correction to the binding energy changes by -4.5×10^{-5} a.u. that is about 1.25% of the experimental binding energy (at $R = 4.63$ a.u.). This change should be compared with the change in binding energy due to correlation, the latter change being only a few per cent of the experimental binding energy. This indicates that relativistic effects play a rather prominent role in determining the shape of the energy surface for this molecule, and any successful explanation of the electronic structure of Be₂ should be based on a relativistic theory.

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