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Author
Lee, Yoon S.

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Yoon S. Lee, Walter C. Ermler, Kenneth S. Pitzer
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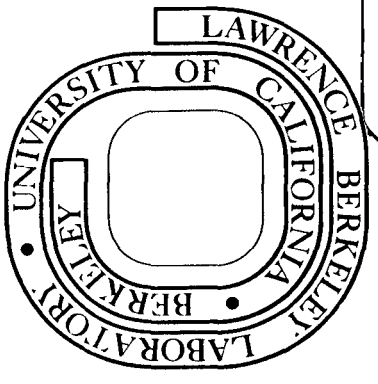

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Ab Initio Effective Core Potentials Including Relativistic Effects. III. Ground State Au_2 Calculations

Yoon S. Lee, Walter C. Ermler[a], and Kenneth S. Pitzer

Department of Chemistry and Lawrence Berkeley Laboratory
University of California, Berkeley, CA 94720

and

A. D. McLean

IBM Research Laboratory
San Jose, CA 95193

[a] Present Address: Department of Chemistry and Chemical Engineering
Stevens Institute of Technology
Hoboken, N.J. 07030

Abstract

SCF calculations have been carried out for the ground $^1\Sigma_g^+(0_g^+)$ state of Au_2 using a variety of *ab initio* effective core potentials (EP). The effective core potentials studied include both a two-component relativistic EP (REP), that includes spin-orbit effects; also averaged relativistic EP (AREP) and a non-relativistic EP (NREP). All-electron non-relativistic calculations were also performed. The values of spectroscopic constants obtained from these calculations indicate that relativistic effects account for a decrease in R_e of over 0.3 Å and an increase in the bond energy of the order of 1 eV. Various intercomparisons indicate the general validity of effective potential methods, properly applied, but also show certain limitations. In particular the NREP results agree well with the all-electron, non-relativistic calculations. Also various relativistic effective-potential methods agree for SCF calculations provided both the basis sets and the EP are carried to sufficiently high order in angular quantum number. The bond distance calculated relativistically agrees very well with experiment.

I. Introduction

In the first paper of this series[1] (hereafter Paper I) the general basis was established for a treatment of molecules containing heavy atoms by relativistic quantum mechanics and effective potentials (EP). This treatment parallels the ab initio core potential methods based on non-relativistic quantum mechanics as developed recently by several authors.[2] Our procedure starts with the fully relativistic Dirac-Hartree-Fock treatment of each atom. Thus the EP derived from these atomic data contains all relativistic effects on the core electrons as well as the valence electrons except for Breit interactions and are labelled REP. The results include spin-orbit effects and follow the j-j coupling system, i.e., there are separate EP for $p_{1/2}$ and $p_{3/2}$ states, etc. In Paper I the REP were derived for xenon and gold atoms. In this paper we use the results for gold to treat the ground state of Au_2 in the SCF and MCSCF approximation and compare the results with those from an all-electron nonrelativistic treatment, with more approximate relativistic calculations, and with experiment. A paper to follow will present calculations for excited states, as well as the ground state, of Au_2 based on extensive configuration interaction.

Rigorous relativistic molecular calculations must be made in the ω-ω coupling system (equivalent to j-j coupling for atoms). Although we are developing programs for diatomic molecules in ω-ω coupling for configurations with open shells, these are not complete and hence not available for the present

calculations. A SCF calculation was made, however, for the single configuration closed shell ground state of Au_2 with two-component relativistic spinors and EP's.

A further approximation allows the use of molecular programs in L-S coupling; this requires the deletion of spin-orbit coupling. We have followed this method by taking the weighted average of the two EP's for a given non-zero ℓ value, i.e., for $p_{1/2}$ and $p_{3/2}$ or $d_{3/2}$ and $d_{5/2}$. Such results are labeled AREP for "averaged relativistic effective potentials." There are semi-empirical methods for the approximate re-introduction of spin-orbit effects.[3] Paper II[4] presents results by this method for Xe_2 in the ground and excited states and for Xe_2^+. Kahn, Hay, and Cowan[5] have also developed a method for AREP calculations in which they start with partially relativistic atomic calculations which, in the Pauli approximation, include only the mass-velocity and Darwin terms and omit the spin-orbit term. Comparison of results from the two AREP methods shows little difference between them; hence, one concludes that the additional approximations of Kahn, et al., are not important in this case, at least.

II. Calculations

The EP's for Au were obtained using the methods described in Paper I. Programs to compute the necessary molecular integrals over the original numerical EP with respect to a basis set of Slater-type functions (STF) were developed based on an earlier program that employed a zeta-function approach.[6]

In addition, non-relativistic (NREP) and averaged relativistic (AREP) SCF calculations have been carried out using EP's derived[7] using the methods of Refs. 2 and 5 for Au expressed as fits to Gaussian-type functions together with corresponding[7] valence electron basis sets. Finally, to gauge the EP approximation of the core electrons, all-electron SCF calculations were carried out for Au_2.

A. Calculations with AREP and NREP

It is instructive to describe certain features of the program[6] used to compute the matrix elements over the EP with respect to an STF basis. An advantage in using numerical integration procedures is that it allows us to input the EP in any convenient form, viz as numerical functions, or as fits to Slater (STF) or Gaussian (GTF) functions, from which the appropriate quadrature points may be generated internally. The numerical EP's computed by the methods of Paper I, being relative to the logarithmic grid dictated by the numerical Dirac Hartree-Fock procedure, are matched with the Gauss-Legendre or Gauss-Laguerre quadratures used by the EP integral program by interpolation using a cubic spline technique.

In the case of the relativistic EP's the behavior in the region near the nucleus has been accounted for by matching the expected behavior [Paper I, Eq (43)] as $r \to 0$ with the value and its first derivative of the EP at some value r_{min} where the EP is still well-behaved, i.e., numerical inaccuracies have not yet become evident.

The questions to be addressed here involve the problems inherent in the representation of the EP's for a given atom in the various forms that derive from the general equation[2]

$$U^{AREP} = U_L^{AREP} + \sum_{\ell=0}^{L-1} (U_\ell^{AREP} - U_L^{AREP}) |\ell m><\ell m| . \qquad (1)$$

In this part we treat only those EP's that correspond to the use of LS-coupling in the molecular calculations. Relativistic EP's generated by the method described in Paper I have been transformed to the appropriate form by taking the weighted average of the two components corresponding to a given value of the angular quantum number ℓ. These averaged relativistic effective core potentials (AREP) yield good results for Xe_2 ground, excited, and positive ion states[4] and compare well with results[8] based on the AREP of Kahn et al.[5] The value of L corresponding to the largest angular momentum used in deriving U^{EP} defines the "residual potential" and is, ideally, one greater than the highest ℓ of the core.

We made SCF calculations for Au_2 based upon our AREP functions, which are designated AREP(I), and upon the AREP obtained by Hay, et al,[7] for gold by the method of Kahn, et al,[5] which omits spin-orbit effects in the atomic calculations; the latter results are designated AREP(II). We also used the non-relativistic EP of Hay, et al,[7] for calculations on Au_2 listed as NREP. For AREP(II) and NREP we used the basis sets chosen by Hay, et al.[7]

B. Calculations with REP

The application of the j-dependent relativistic effective core potentials (REP) to molecular calculations requires the computation of matrix elements over a basis set of two-component spinors corresponding to four-component Dirac spinors without small components. The Hamiltonian is expressed as

$$H = \sum_{\mu=1}^{n_v} h_\mu + \sum_{\mu \neq \nu} \frac{1}{r_{\mu\nu}} \tag{2}$$

where n_v is the total number of valence electrons and $r_{\mu\nu}$ is the distance between electron μ and ν. In Eq (2) h_μ is given by

$$h_\mu = -\frac{1}{2}\nabla_\mu^2 + \sum_{\alpha=1}^{N} \left[-\frac{Z_\alpha}{r_{\alpha\mu}} + U_\alpha^{REP}\right] \tag{3}$$

where Z_α is the nuclear charge of nucleus α, U_α^{REP} can be approximated by [Paper I, Eq (41)] and N is the number of nuclei.

$$U_\alpha^{REP} = U_{LJ}^{REP}(r_{\alpha\mu}) + \sum_{\ell=0}^{L-1} \sum_{j=|\ell-\frac{1}{2}|}^{\ell+\frac{1}{2}} \sum_{m=-j}^{j} [U_{\ell J}^{REP}(r_{\alpha\mu}) - U_{LJ}^{REP}(r_{\alpha\mu})] |\ell jm\rangle_\alpha \langle \ell jm|_\alpha \tag{4}$$

where the projection operators are defined by

$$|\ell jm\rangle\langle \ell jm| = \left[\sum_{\sigma=\pm\frac{1}{2}} C(\ell\tfrac{1}{2}j;\ m-\sigma,\ \sigma)|Y_\lambda^{m-\sigma}(\theta,\phi)\phi_{1/2}^{\sigma}\rangle\right] x$$

$$\left[\sum_{\sigma'=\pm\frac{1}{2}} C(\ell\tfrac{1}{2}j;\ m-\sigma',\ \sigma')\langle Y_\lambda^{m-\sigma'}(\theta,\phi)\phi_{1/2}^{\sigma'}|\right] \tag{5}$$

with the notation the same as in Paper I. All one and two

electron matrix elements of the above Hamiltonian with two component basis functions can be expressed as linear combinations of appropriate non-relativistic integrals. The detailed expressions for these matrix elements may be obtained from the work by Malli and Oreg[9] by eliminating parts dependent on the small components of the Dirac spinors.

Matrix elements over angular projection operators [Eq (5)] are calculated as linear combinations of the non-relativistic integrals described in the previous section and additional integrals that correspond to the case $\sigma \neq \sigma'$. The formalism for the SCF procedure is essentially parallel to that developed by Malli and Oreg for relativistic theory for closed-shell molecules.[9] Although their formalism is limited to the minimal basis set representation of the Dirac-Hartree-Fock calculations, this restriction disappears in our application because of the absence of small components. The symmetry properties of these molecular orbitals are the same as those of the relativistic molecular orbitals, viz. orbitals are only distinguished by their total angular momentum like Hund's case (c).

At present, the program is limited to closed shell configurations of diatomic molecules.

C. All-electron Non-relativistic Calculations

A double-zeta basis set generated for the $(\ldots 5d^9\ 6s\ 6p)\ ^4F$ state of the gold atom was used in single configuration SCF calculations on $(\ldots 27\sigma^2 \ldots . 16\pi^2 \ldots . 8\delta^2 \ldots 2\phi^2)\ ^1\Sigma_g^+\ Au_2$. The

atomic energy with this basis set is -17864.62328 a.u. compared with a value of -17864.62372[10] for a thoroughly optimized double-zeta basis. Simply because of the large number of occupied shells, these double zeta bases for heavy atoms are better able to contain orbital expansions which approach the Hartree-Fock limit than is the case in light atoms, at least for s and p symmetries. Also because of the large number of occupied shells, the basis set contains, without further addition, functions whose extent and symmetry type are those required for describing polarization effects in the molecular environment. The results of this double-zeta Au_2 calculation, then, will be close to the Hartree-Fock limit for the shape of the interaction potential. The energy difference between R = 20. bohr and R = 5. bohr should be within ~0.2 eV of the Hartree-Fock limit. Absolute energies, of course, will have very much larger errors, but this is inconsequential.

III. Results and Discussion

Presented in Tables I and II are a series of results for the ground $^1\Sigma_g^+$ state of Au_2. The calculations are single configuration SCF (Table I) and two-configuration MCSCF (Table II) where the σ_u^2 term necessary for the proper description of two ^2S atomic states at dissociation has been included. The 2s2p2d1f basis set used in our EP calculations is given in Table III. Since the SCF wavefunctions for Au_2 do not allow for the proper asymptotic behavior, dissociation energies are not available. Instead we report the values of $(E_{20}-E_e)$, the decrease in total SCF energy from $20\ ^{a.u.}/$ to the minimum at R_e. These values may be used for comparison among the SCF calculations, but it should be noted that the tendency for these wavefunctions to admixtures of atom pair and ion pair limits may not have proceeded to the same extent at $R = 20.0\ ^{a.u.}/$ for all of the cases. Hence, the D_e values for the SCF results should only be taken as qualitative comparisons. The values of R_e and ω_e, on the other hand, should be consistently represented and were derived using five points near R_e.

The SCF calculations are intended to show the degree of consistency of the use of EP's derived from different formalisms (Refs. 1, 2, and 5) and to give an indication of the magnitude of the relativistic effects in Au_2. Table I shows the agreement between the all-electron and valence electron non-relativistic EP (NREP) results to be quite reasonable. The differences (Rows 1 and 2) between values of R_e, $(E_{20}-E_e)$,

and ω_e are 0.01 Å, 0.14 eV and 14 cm^{-1}, respectively. Similarly, the relativistic calculations AREP(I) and REP using a L=4 residual potential and a numerical form of U_ℓ determined by the methods of Paper I yield results (Rows 4 and 5) in good agreement with each other and with those from AREP(II) in Row 3. This agreemenet between AREP and REP indicates that the averaging procedure is reasonable for this case.

Thus, it appears from the results of Table I that the relativistic effects in Au_2 yield a decrease in R_e in excess of 0.3 Å and about a 25% increases in ω_e. The relativistic calculations of R_e are in excellent agreement with the experimentally determined[11] value R_e = 2.47 Å. The relativistic calculations for ω_e are smaller than the experimental value of 191 cm^{-1} but much closer than the non-relativistic results. The energy values in Table I are not so clearly interpretable, but they indicate a relativistic increase in bond energy of the order of 1 eV.

Orbital energies at R = 4.75 a.u. are shown in Fig. 1. Comparing $6s\sigma_g$ orbital energies one may conclude that 6s electrons are responsible for most of relativistic effects in Au_2, a large increase in binding energy from the non-relativistic to the relativistic values. The 5d orbital energies are decreased slightly from the non-relativistic values to those of AREP(I), but this effect is small as compared to the splitting from either interatomic interaction or the spin orbit effect (in REP). Orbitals of a given ω value in the last column arise from different λ values in the other columns, i.e.,

ω = 1/2 from either σ or π and ω = 3/2 from either π or δ. Consequently, there can be some mixing of these 1/2 or 3/2 orbitals and the differences of individual REP values from AREP(I) values are not pure spin-orbit effects, although that was the basic cause.

Wavefunctions for Au_2 including more extensive configuration mixing have been computed[12] using the numerical AREP and the same valence STF basis set for all electronic states arising from the atomic asymptotic limits $^2S + {}^2S$ and $^2S + {}^2D$. The improved ground state potential energy curve has R_e = 2.37 Å, D_e = 2.27 eV, and ω_e = 165 cm^{-1} in good agreement with the experimentally determined values.

Table II presents comparisons of properties of Au_2 derived using the AREP(I) defined by the pseudo-orbital transformation for an 11-valence-electron Au atom as detailed in Paper I. There are three principal variances in the calculations of Table II yielding important comparisons. The first is the deletion of the f-type polarization function from the basis set; the second is in the form of the EP as either numerical $U_\ell(r)$'s or STF or GTF least squares fits of these, and the third is in the choice of the residual potential U_L [Eq. (1)] as L = 2, 3, or 4.

The effect of the f-type STF basis function, obtained by comparing rows 2 and 3 with rows 7 and 8, respectively, is about 0.1 eV in D_e and .06 Å in R_e. Since this is a rather substantial effect for the addition of polarization-type functions for mostly non-bonding d orbitals, an appreciable part may be attributed to the superposition problem for a

double-zeta basis set (i.e., a basis function centered on one nucleus alleviating deficiencies in the atomic basis set at the other nucleus.)

The effect of using a least squares fitted AREP as opposed to the original numerical form is seen by comparing Rows 1, 4 and 5. The differences of 0.1 and 0.2 eV in D_e of STF and GTF fitted AREP's from the numerical form is a reasonable reflection of accuracies expected from the fitting method.

The most obvious discrepancy in Table II is that among the calculations where the residual potentials differ. Whereas the changes resulting from choosing L=3 instead of L=4 are small, but not negligible, those due to the use of L=2 are unacceptably large (compare the pairs of rows 1-3, 5-6, and 7-8). The use of U_d as the residual potential for the AREP leads to potential energy curves that are much too attractive with R_e too small by 0.3 Å, and D_e and ω_e too large by about 2 eV and 100 cm^{-1}. This discrepancy is the consequence of the attractive tail in the residual d potential shown in Fig. 2. This problem has also been encountered in other work and corrected by shortening the region of fitting[4,13,14] or by generating the residual potential from highly positive ions.[13] In our case the choice of a sufficiently large L value for the residual potentials yielded satisfactory results, but we cannot as yet draw firm general conclusions on this matter.

In conclusion we note that the calculations reported here show large relativistic effects shortening and strengthening the bond in Au_2 and indicate that the primary source of these changes is in the contraction of the 6s orbitals.

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Table I. SCF Results for Au_2

Basis Set	EP	L_{max}[a]	R_e/Å	$(E_{20}-E_e)$/eV	ω_e/cm^{-1})
STF (12s 10p 6d 2f)	All-electron		2.84	3.00	105
GTF (3s 3p 3d)/[2s 2p 2d]	NREP(GTF)	d	2.83	2.86	91
GTF (3s 3p 3d)/[2s 2p 2d]	AREP(II)(GTF)	d	2.48	4.00	138
STF (2s 2p 2d 1f)	AREP(I)(Numerical)	g	2.48	4.01	145
STF(2s 2p 2d)	REP(Numerical)	g	2.50	3.93	142

[a] See Eq.(1).

Table II. MCSCF Results for Au_2 with AREP(L)

			L_{max}[a]	Re(Å)	D_e(eV)	ω_e(cm^{-1})
1	STF (2s 2p 2d 1f)	AREP(Numerical)	g	2.54	0.95	107
2	STF (2s 2p 2d 1f)	AREP(Numerical)	f	2.50	1.12	120
3	STF (2s 2p 2d 1f)	AREP(Numerical)	d	2.18	3.18	218
4	STF (2s 2p 2d 1f)	AREP(STF)[b]	g	2.56	0.85	111
5	STF (2s 2p 2d 1f)	AREP(GTF)[c]	g	2.56	0.76	107
6	STF (2s 2p 2d 1f)	AREP(GTF)	d	2.19	1.49	174
7	STF (2s 2p 2d)	AREP(Numerical)	f	2.56	1.02	116
8	STF (2s 2p 2d)	AREP(Numerical)	d	2.24	2.90	195

[a] See Eq. (1).

[b] Ref. 1.

[c] Ref. 15.

Table III. Slater basis set of Au for the REP[a] and AREP(I) calculations

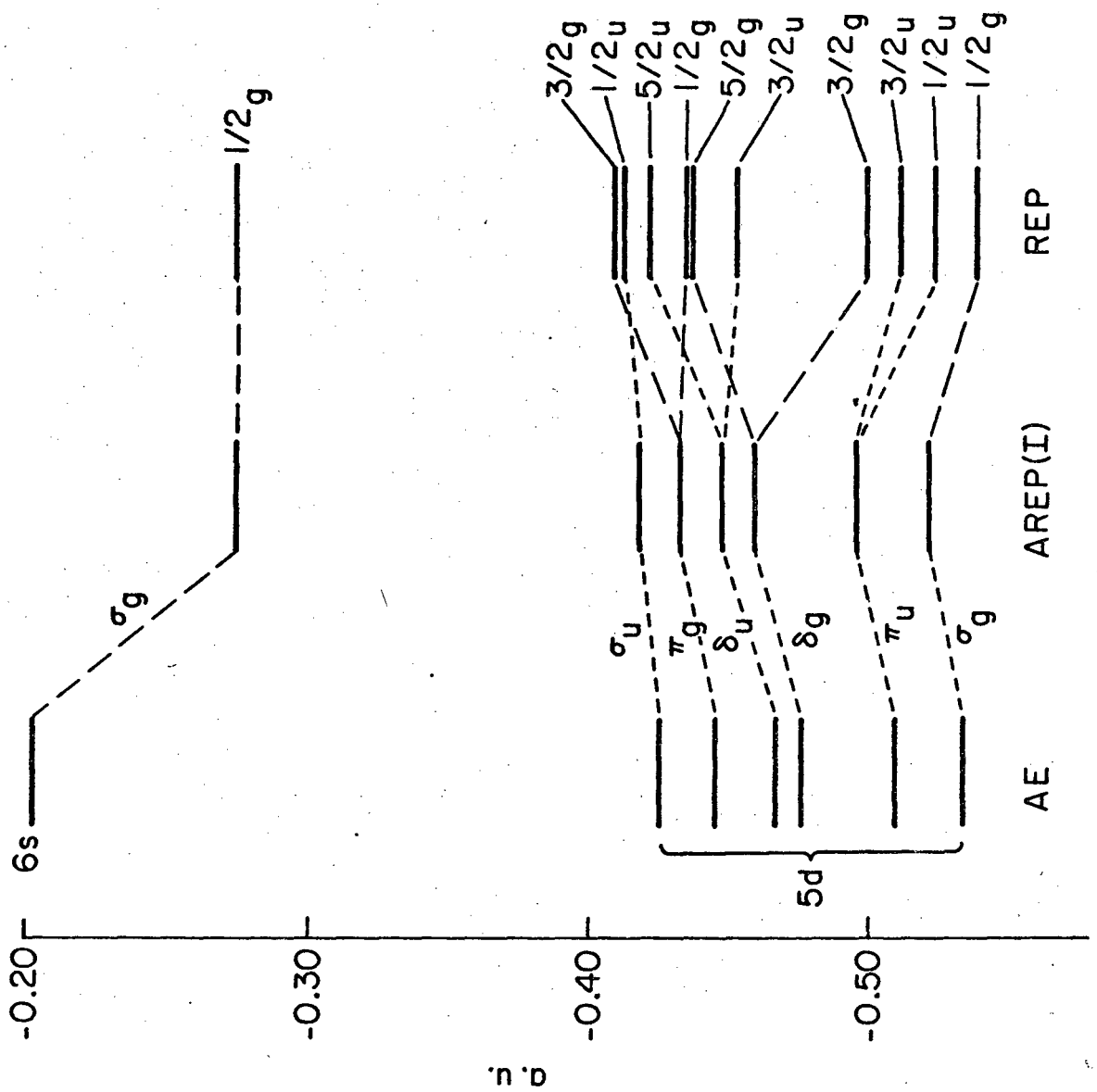
ℓ	n	ζ
s	2	1.17
	2	0.75
p	2	0.82
	2	0.41
d	3	2.40
	3	1.26
f	4	2.00

[a] Identical basis functions were used for $j = \ell - \frac{1}{2}$ and $j = \ell + \frac{1}{2}$ orbitals with the same ℓ.

Figure Captions

Figure 1. Orbital energies (in a.u.) of Au_2 calculated at R = 4.75 a.u. AE, AREP and REP refer to the all-electron, the averaged relativistic EP and the relativistic EP, respectively. Lines connecting the orbital energies calculated with AREP(I) and REP indicate the probable correlations of the ω-ω coupled orbitals.

Figure 2. Relativistic effective core potentials (REP) of the 11-valence electron Au.


-0.20
-0.30
-0.40
-0.50
a. u.
6s
σg
1/2g
5d
σu
πg
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δg
πu
σg
3/2g
1/2u
5/2u
1/2g
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1/2u
1/2g
AE
AREP(I)
REP

Fig. 1

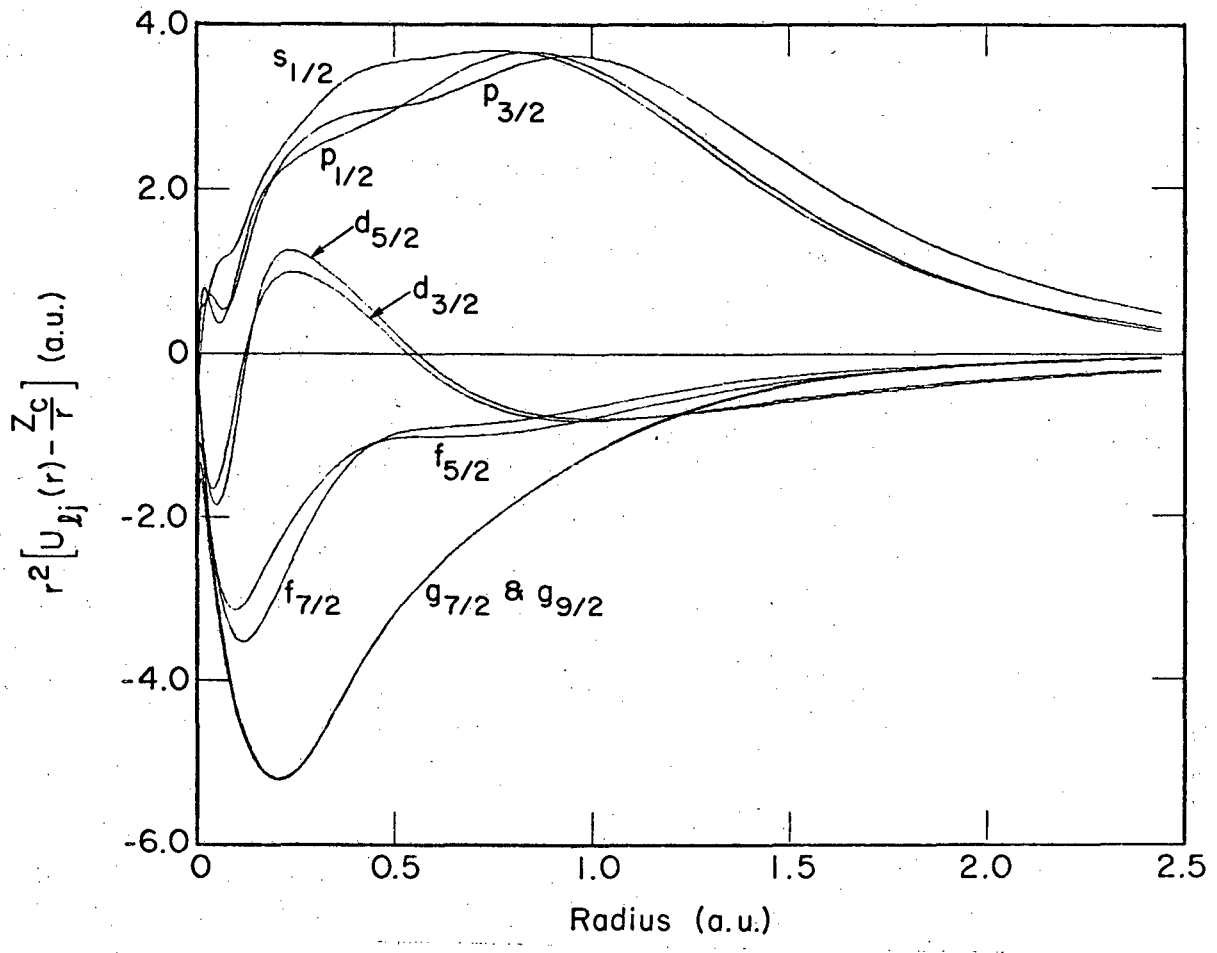
4.0
2.0
0
-2.0
-4.0
-6.0
0
0.5
1.0
1.5
2.0
2.5
Radius (a.u.)
$r^2\left[U_{lj}(r)-\frac{Z_c}{r}\right]$ (a.u.)
$s_{1/2}$
$p_{3/2}$
$p_{1/2}$
$d_{5/2}$
$d_{3/2}$
$f_{5/2}$
$f_{7/2}$
$g_{7/2}$ & $g_{9/2}$

Fig. 2

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