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Improved Ab Initio Effective Potentials for Ar, Kr, and Xe

with Applications to their Homonuclear Dimers

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Abstract

Effective core potentials for the Ar, Kr, and Xe atoms derived from numerical Hartree-Fock and Dirac-Hartree-Fock wavefunctions are applied in SCF and CI calculations of homonuclear diatomic potential energy curves. Detailed comparisons are made with the all-electron calculations of Wadt for the ground and lowest positive states. Relativistic effects, excluding spin-orbit coupling, are seen to be relatively unimportant. Plots of the potential energy curves and computed spectroscopic constants show excellent agreement with the all-electron results. On the other hand, comparisons with results obtained using effective potentials derived using variants of Phillips-Kleinman procedures show dramatic differences for Xe_2 and Xe_2^+ . From SCF calculations on Xe_2 and Xe_2^+ it was found that the explicit inclusion of the spin-orbit operator in the SCF procedure (using ω - ω coupling) results in essentially the same potential curves obtained by adding the spin-orbit correction as a final semi-empirical perturbation.

Introduction

Though numerous procedures have been developed for replacing the core electrons in molecular calculations with effective potentials (EP) or pseudopotentials,¹⁻⁵ relatively little work has been done to evaluate the reliability of such procedures for molecular calculations. Furthermore, when the appropriate comparisons have been made, the results were usually disappointing. Kahn, et al.⁵ and later Hay et al.⁶ compared dissociation curves computed using the EP procedure developed by Kahn and co-workers, with curves computed from all-electron (AE) wavefunctions. For the halide dimers they found that the Kahn procedure (based on a Phillips-Kleinman transformation¹ of atomic orbitals) tended to seriously underestimate the inner repulsive components of the potential curves. More recently, Das⁷ compared the dissociation curves for Cs_2^{++} computed using his pseudopotential method (also based on the Phillips-Kleinman transformation) with AE curves and concluded that such procedures "suffer from a fundamental deficiency" relative to the full calculations. Gropen et al.,⁸ after comparing dissociation curves computed using the pseudopotential procedure developed by Bonifacic and Huzinaga³ with accurate AE results, stated that their "results for I_2 indicate possible difficulties with increasing nuclear charge".

Although comparisons have been made for F_2 and Cl_2 showing excellent agreement between AE dissociation curves and curves computed using the procedure proposed by Christiansen, Lee and Pitzer,⁹ until now no such test has been performed for molecules containing heavier elements. It was shown by Christiansen et al. that the Phillips-Kleinman (PK) pseudo-orbitals employed in the formalisms of Kahn and others differ significantly from the corresponding atomic Hartree-Fock (HF) orbitals (or Dirac-Fock spinors) in the valence region leading to errors in subsequent molecular

calculations. These problems can be avoided by replacing the PK pseudo-orbital by one which matches precisely the atomic HF orbital in the valence region and differs significantly from the atomic orbital (or spinor) only in the region close to the nucleus. Detailed descriptions of the procedures used to obtain such pseudo-orbitals are given in references 9 and 10.

In the following sections we will present comparisons of dissociation curves obtained using the above EP formalism, with the AE calculations of Wadt¹¹ for the ground states of the Ar, Kr and Xe dimers and dimer ions. Comparisons are made at both the SCF and CI levels. For Kr and Xe further comparisons are made using the relativistic effective-potentials (REP) generated by essentially the same formalism. Finally, schemes for introducing spin-orbit coupling are briefly examined.

Effective Core Potentials

In all of the present EP calculations only eight electrons (the outer two s and six p electrons) on each atom were treated explicitly. The non-relativistic s and p type EPs were generated using the formalism described in reference 9, from ground state numerical atomic calculations.¹² The Ar d symmetry EP, and Kr d and f symmetry EPs were generated in a similar manner from atomic wavefunctions in which a single valence s electron had been excited into a low-lying d or f orbital to form 3D or 3F states. The d and f symmetry EPs for Xe were obtained from atomic calculations in which a 5p electron was excited into either a 5d or 4f orbital which was subsequently optimized for the average configuration energy.¹² Our relativistic $s_{1/2}$, $p_{1/2}$ and $p_{3/2}$ EPs (REP) for Kr and Xe were generated in the same way but from Dirac-Fock wavefunctions.¹³ (That is, pseudospinors were obtained from Dirac-Fock spinors using

the procedure of Christiansen et al.^{9,10} The REPs are then generated using the formalism of Lee et al.¹⁴) The $d_{3/2}$, $d_{5/2}$, $f_{5/2}$ and $f_{7/2}$ REPs were obtained by exciting a single $p_{3/2}$ electron into the appropriate d or f type spinor and optimizing the spinor for the average configuration energy. For most of our molecular calculations the p, d, and f REPs were averaged to eliminate the spin-orbit (SO) operator. The resulting averaged REPs (AREP) can be used in conventional nonrelativistic calculations. The SO effects may then be added as a final perturbation.

Basis Sets

Once the effective potentials were formed, triple-zeta s and p type STO basis sets were generated for each of the five potentials by optimizing the exponents in atomic ground state calculations for which the core electrons had been replaced by the appropriate EPs or AREPs. To each set a single set of 3d type polarization functions was added whose exponents were crudely optimized for the equilibrium geometry of the corresponding dimer ion using the non-relativistic EPs to replace the core electrons. Thus, for Kr and Xe the same d functions were used for both the EP and AREP molecular calculations.

Calculations and Results

In Figures 1 through 3 are plotted dissociation curves for the ground states of the neutral dimers and positive dimer ions of Ar, Kr, and Xe. These curves were obtained using the POL CI procedure (for the neutral dimer this corresponds to an SCF calculation) as described by Wadt.¹¹ For Kr and Xe the calculations were performed using the AREPs as well as the non-relativistic EPs. The Appendix contains the valence energies for the solid curves given in Figures 1-3. For comparison the

corresponding curves obtained from non-relativistic all-electron calculations by Wadt¹¹ are included. The EP and AE curves are almost superimposable. The largest deviations are about 0.1 eV. Furthermore this may be as much due to basis set variations as it is to the EP approximations; the number of AO's as well as virtual MO's is much smaller for the EP calculations. Notice that for small values of R the AREP curves for Kr and Xe are slightly less repulsive relative to the AE or EP curves. This is due to the relativistic contraction of the electron distribution. In Table I are listed spectroscopic constants for the three dimer ions obtained from EP, AREP and AE calculations. For all three molecules there is excellent agreement between the EP and AE values. Notice again the slightly shorter R_e values obtained from the Kr and Xe AREP calculations as compared to the non-relativistic EP values. However, this shift is still less than 0.05 Å and is for most purposes negligible.

In Figures 4 and 5 the present EP results for Xe_2 and Xe_2^+ are compared with previous EP and AREP curves generated by Wadt¹⁵ and with AREP curves obtained by Ermler et al.¹⁶ (the neutral curves are from SCF and the ion curves from POL CI¹⁵ and SCF¹⁶ calculations). Wadt's AE curves have been added for comparison. For the neutral dimer the errors in the repulsive walls of the potential curves obtained from the Wadt EP and Ermler AREP calculations are on the order of one eV. A similar error is seen for the ion where the equilibrium distance is shifted in about .1 Å. The corresponding spectroscopic constants for the ion are listed in Table II for comparison.

Spin-orbit Coupling

Though, as seen in Figures 2 and 3, the relativistic contraction of the electron distribution has only a slight effect on the neutral or ion

dissociation curves, the spin-orbit effects for the ion are substantial. The spin-orbit splitting for the Xe 5p shell is more than one eV. Using the present REPs SO coupling may be included explicitly in SCF calculations,¹⁷ however, its inclusion in CI calculations is complicated. In previous work Wadt opted to incorporate SO effects via an atoms-in-molecule approach.¹¹ In this procedure SO parameters are obtained empirically from the atomic ion and then added to the diagonal matrix of molecular ion energies, which is subsequently rediagonalized for the various inter-nuclear separations in question. In Figure 6 are plotted Wadt's AE curves (including the semi-empirical SO correction)¹¹ for the $I(1/2)_u$, $II(1/2)_u$, and $(3/2)_u$ states of Xe_2^+ along with similarly generated curves using the present AREP. To determine the validity of the semiempirical SO procedure, the SCF dissociation curve for the $I(1/2)_u$ state of Xe_2^+ was computed in full $\omega-\omega$ coupling ($\omega\omega$ SCF) using the present REP and compared to the analogous SCF curve obtained in LS coupling using the present AREP with the SO corrections added semiempirically as before. These two curves are superimposable to within .0005 au indicating that the atoms-in-molecules approach is an excellent approximation for the molecules in question. Spectroscopic data for these two calculations are listed in Table III along with results for the two $I(1/2)_u$ curves from Figure 6.

Discussion

Clearly the effective potential procedure employed here is capable of reliably reproducing the results of all-electron calculations even for states which differ considerably in their electron configurations from those for which the EPs were generated. Furthermore, since this procedure differs from that employed by Ermler et al.¹⁶ only in the

definition of the pseudo-orbital, the errors in previous work must be related to the use of the Phillips-Kleinman transformation. As stated above, the important difference between Phillips-Kleinman pseudo-orbitals and those used in the present calculations is that the Phillips-Kleinman pseudo-orbitals underestimate the electron density in the valence region by as much as 10% to 30% relative to atomic Hartree-Fock orbitals or Dirac-Fock spinors. Since in practice the pseudo-orbital represents that portion of the atomic electron density which will be treated explicitly in any subsequent atomic or molecular calculation, the remainder is, in effect, frozen into the core. It has been shown previously⁹ that this results in an excessively attractive tail in the EP and ultimately in molecular interaction potentials which seriously underestimate the repulsive portion of the dissociation curves.⁵ An obvious manner in which this type of error might occur is as follows. In molecular calculations employing EPs the two-center valence-valence interactions (as defined by the pseudo-orbitals) are treated explicitly and the valence-core interactions are presumably accounted for by the effective potential. However, the two-center core-core interactions are obtained by assuming that the cores are made up of spherical non-overlapping charge distributions. Thus the potential between two such cores is a simple point charge interaction, $Z_a Z_b / R_{ab}$. However, due to Pauli type interactions this approximation will seriously underestimate the repulsive interaction if the two spheres appreciably overlap. Such an occurrence is unavoidable, at least for short bond distances, with Phillips-Kleinman pseudo-orbitals. Due to the fact that tail character is no longer being mixed into the core the present definition of the pseudo-orbital decreases significantly the internuclear separations at which such errors might occur.

Another possible source of error relates particularly to the use of pseudopotentials such as those developed by Das⁴ which contain core projection operators explicitly. The purpose of these operators in the original Phillips-Kleinman formalism⁵ is to prevent the core orbitals from being occupied by raising their energies up to the valence level. In subsequent calculations this could lead to wavefunctions for excited states or molecular bonds with considerable "core" character and could therefore lead to problems with basis sets. Although the formalism developed by Bonifacic and Huzinaga³ is not explicitly derived from the Phillips-Kleinman procedure, the core projection operators are employed in a roughly similar manner. Most Phillips-Kleinman type effective potential schemes avoid this problem when the radial projector is replaced by a local operator.⁵

In conclusion it has been demonstrated that effective potentials generated in the manner described by Christiansen *et al.*⁹ are highly reliable in particular relative to other methods currently in use. This has been shown to be consistently the case even for ionized states of molecules containing heavier atoms.

Acknowledgments

We thank W. R. Wadt for providing us with the individual energy points for the dissociation curves reported in Ref. 11.

This work was partially supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy through Contract W-7405-ENG-48. One of us (WCE) acknowledges the Research Corporation and the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support.

Appendix: Valence Energies of Rg_2 and Rg_2^+ using EP's and AREP's in a POL-CI Procedure (bond lengths and energies in atomic units.)

Ar_2 (SCF) $1_{\Sigma_g^+}$		Kr_2^+ AREP CI $2_{\Sigma_u^+}$		Xe_2 (SCF) $1_{\Sigma_g^+}$ (AREP)	
3.0	-40.7135	4.25	-35.7048	4.5	-30.2514
4.0	-41.3140	4.5	-35.7355	5.0	-30.4007
4.25	-41.3632	4.75	-35.7519	5.5	-30.4740
4.5	-41.3954	5.0	-35.7593	5.75	-30.4950
4.75	-41.4162	5.25	-35.7613	6.0	-30.5097
5.0	-41.4296	5.5	-35.7600	6.25	-30.5199
5.25	-41.4381	6.0	-35.7530	6.5	-30.5269
5.5	-41.4436	7.0	-35.7375	6.75	-30.5318
5.75	-41.4470	8.0	-35.7277	7.0	-30.5351
6.0	-41.4492	9.0	-35.7222	7.5	-30.5390
7.0	-41.4523			8.0	-30.5408
8.0	-41.4527			9.0	-30.5420
10.0	-41.4528			10.0	-30.5422
		Kr_2 EP SCF $1_{\Sigma_g^+}$			
		4.25	-35.6989		
		4.5	-35.7609		
		4.75	-35.8035		
		5.0	-35.8326		
		5.25	-35.8523		
		5.5	-35.8654		
		5.75	-35.8743		
		6.0	-35.8801		
		6.5	-35.8864		
		7.0	-35.8892		
		8.0	-35.8908		
		9.0	-35.8911		
		10.0	-35.8911		
Ar_2^+ $2_{\Sigma_u^+}$ (CI)				Xe_2^+ (CI) $2_{\Sigma_u^+}$ (AREP)	
3.0	-40.5598			4.5	-30.0266
4.0	-40.9558			5.0	-30.1246
4.25	-40.9733			5.5	-30.1594
4.5	-40.9800			5.75	-30.1653
4.75	-40.9806			6.0	-30.1670
5.0	-40.9778			6.25	-30.1662
5.25	-40.9733			6.5	-30.1639
5.5	-40.9683			6.75	-30.1608
5.75	-40.9633			7.0	-30.1573
6.0	-40.9587			7.5	-30.1505
7.0	-40.9454			8.0	-30.1446
8.0	-40.9390			9.0	-30.1364
10.0	-40.9350			10.0	-30.1322
		Kr_2^+ EP CI $2_{\Sigma_u^+}$			
		4.25	-35.4048		
		4.5	-35.4365		
		4.75	-35.4539		
		5.0	-35.4621		
		5.25	-35.4646		
		5.5	-35.4636		
		5.75	-35.4609		
		6.0	-35.4571		
		6.5	-35.4490		
		7.0	-35.4418		
		8.0	-35.4321		
		9.0	-35.4273		
		10.0	-35.4250		
Kr_2 AREP SCF $1_{\Sigma_g^+}$				Xe_2 (SCF) $1_{\Sigma_g^+}$ (EP)	
4.25	-36.0052			4.5	-20.6353
4.5	-36.0647			5.0	-29.7927
4.75	-36.1051			5.5	-29.8716
5.0	-36.1324			5.75	-29.8947
5.25	-36.1508			6.0	-29.9109
5.5	-36.1631			6.25	-29.9223
6.0	-36.1767			6.5	-29.9302
7.0	-36.1851			6.75	-29.9356
8.0	-36.1864			7.0	-29.9394
9.0	-36.1860			7.5	-29.9438
				8.0	-29.9458
				8.5	-29.9467
				9.0	-29.9471
				10.0	-29.9474

Xe_2^+ (CI) $^2\Sigma_u^+$ (EP)

4.5	-29.4209
5.0	-29.5250
5.5	-29.5637
5.75	-29.5708
6.0	-29.5734
6.25	-29.5732
6.5	-29.5712
6.75	-29.5684
7.0	-29.5651
7.5	-29.5583
8.0	-29.5524
8.5	-29.5476
9.0	-29.5441
10.0	-29.5396

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Table I. Spectroscopic constants for Ar, Kr, and Xe dimer ions computed from present EPs^{OR}AREPs and computed from AE results of Ref. 11

	Ar ₂ ⁺		Kr ₂ ⁺			Xe ₂ ⁺		
	EP	AE	EP	AREP	AE	EP	AREP	AE
R _e (Å)	2.46	2.48	2.80	2.78	2.77	3.23	3.19	3.22
D _e (eV)	1.28	1.27	1.13	1.20	1.30	1.05	1.07	1.10
ω _e (cm ⁻¹)	300	292	176	178	186	122	124	124
ω _e x _e (cm ⁻¹)	2.10	1.77	0.80	0.82	0.77	0.40	0.41	0.39

Table II. Xe_2^+ spectroscopic constants obtained from present EP and AREP calculations compared with various EP, REP, AREP and AE results

	EP ^a	AREP ^a	AE ^b	EP ^c	AREP ^c	AREP ^d
R_e (Å)	3.23	3.19	3.22	3.11	3.09	3.03
D_e (eV)	1.05	1.07	1.10	1.04	1.06	1.00
ω_e (cm ⁻¹)	122	124	124	123	125	123
$\omega_e x_e$ (cm ⁻¹)	0.40	0.41	0.39	0.43	0.45	0.47

^a Present results.

^b From Ref. 11.

^c From Ref. 15.

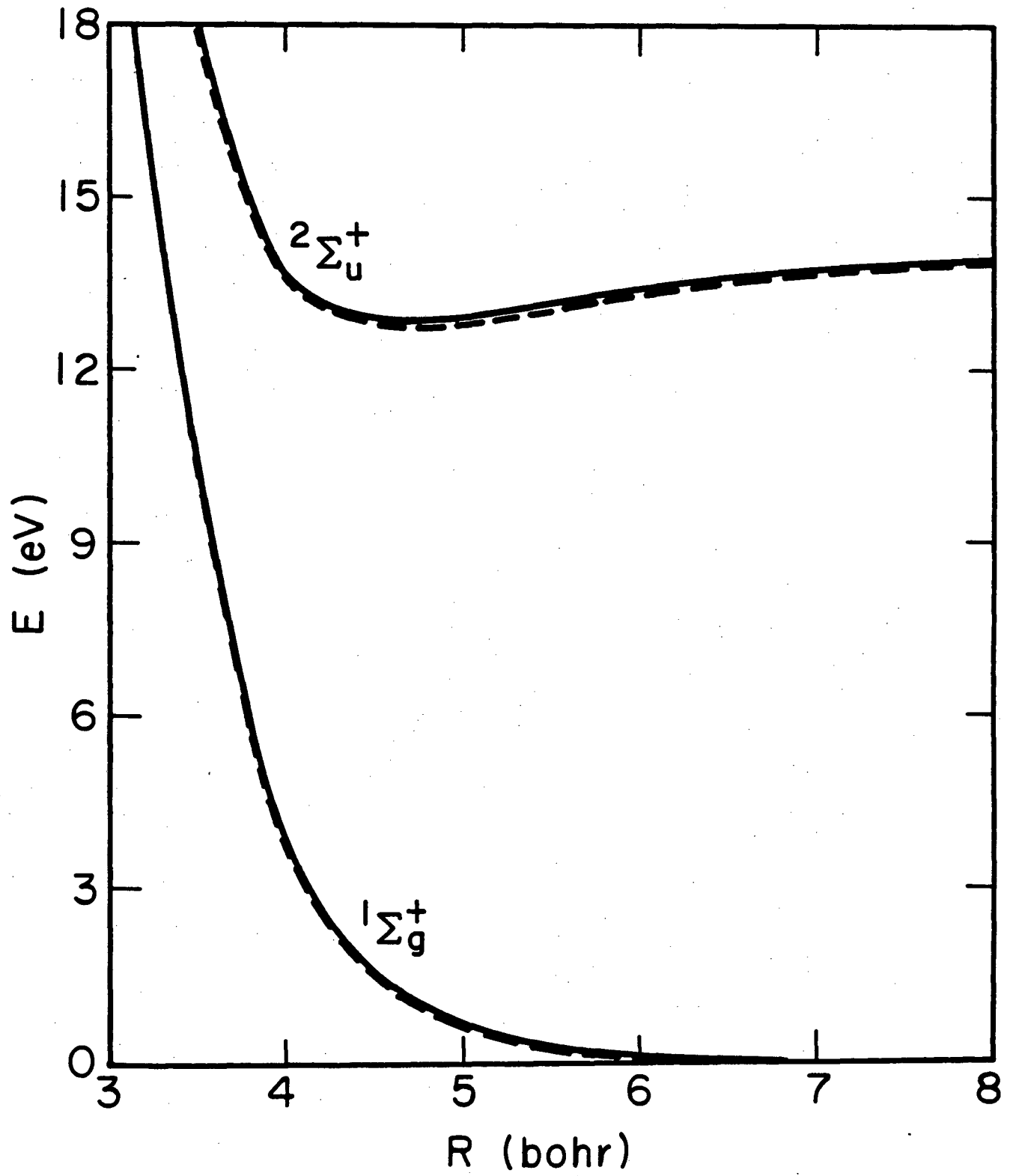
^d From Ref. 16.

Table III. Xe_2^+ spectroscopic constants for the $I(1/2)_u$ state from the present SCF AREP, $\omega\omega$ SCF REP and CI AREP calculations. The AE CI calculations of Ref. 11 have been included for comparison. For all but the $\omega\omega$ SCF calculations the spin-orbit corrections were added semiempirically

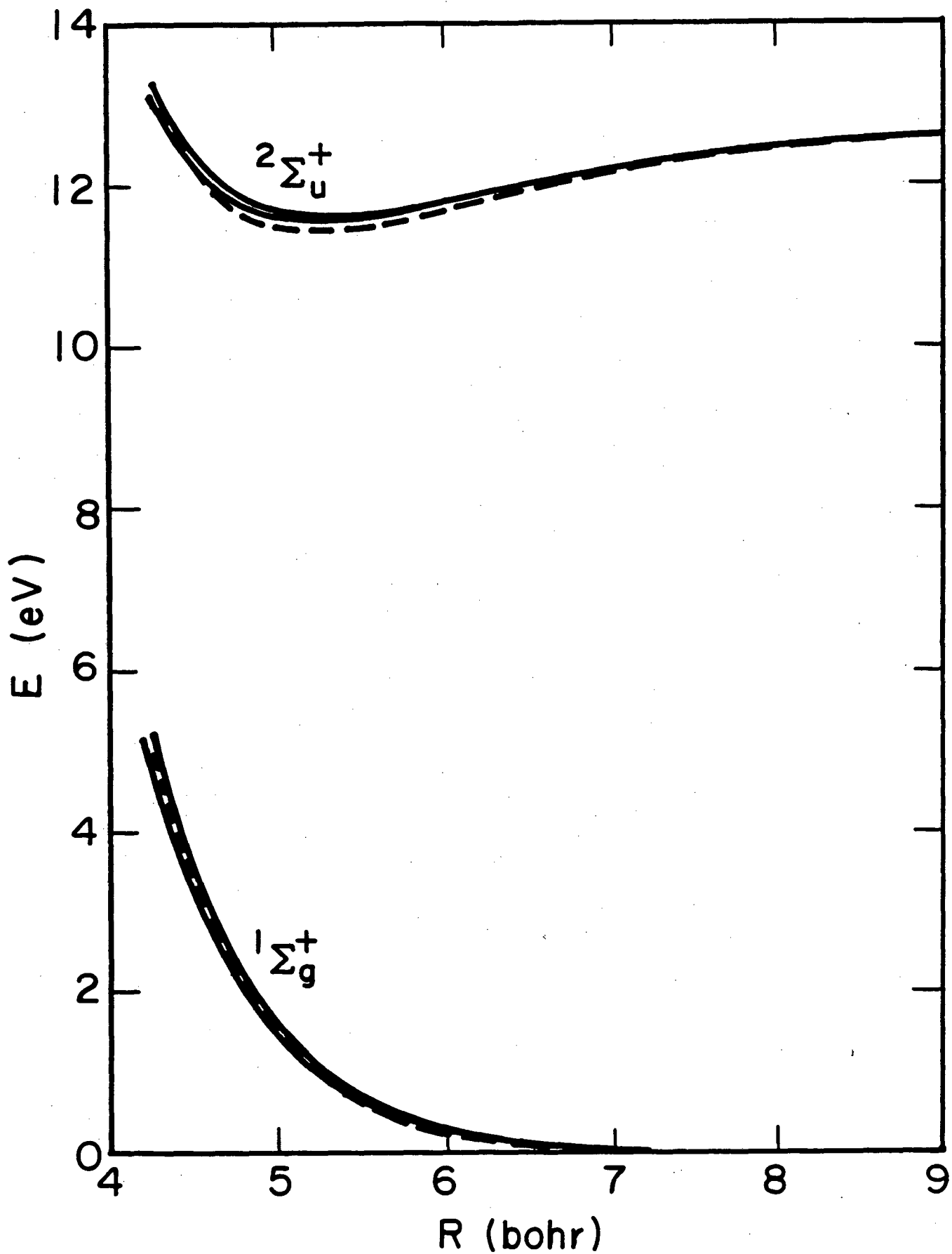
	SCF-AREP	$\omega\omega$ SCF-REP	CI-AREP	CI-AE
R_e (Å)	3.23	3.23	3.23	3.27
D_e (eV)	0.69	0.70	0.77	0.80
ω_e (cm^{-1})	111	110	112	112
$\omega_e x_e$ (cm^{-1})	0.51	0.51	0.48	0.44

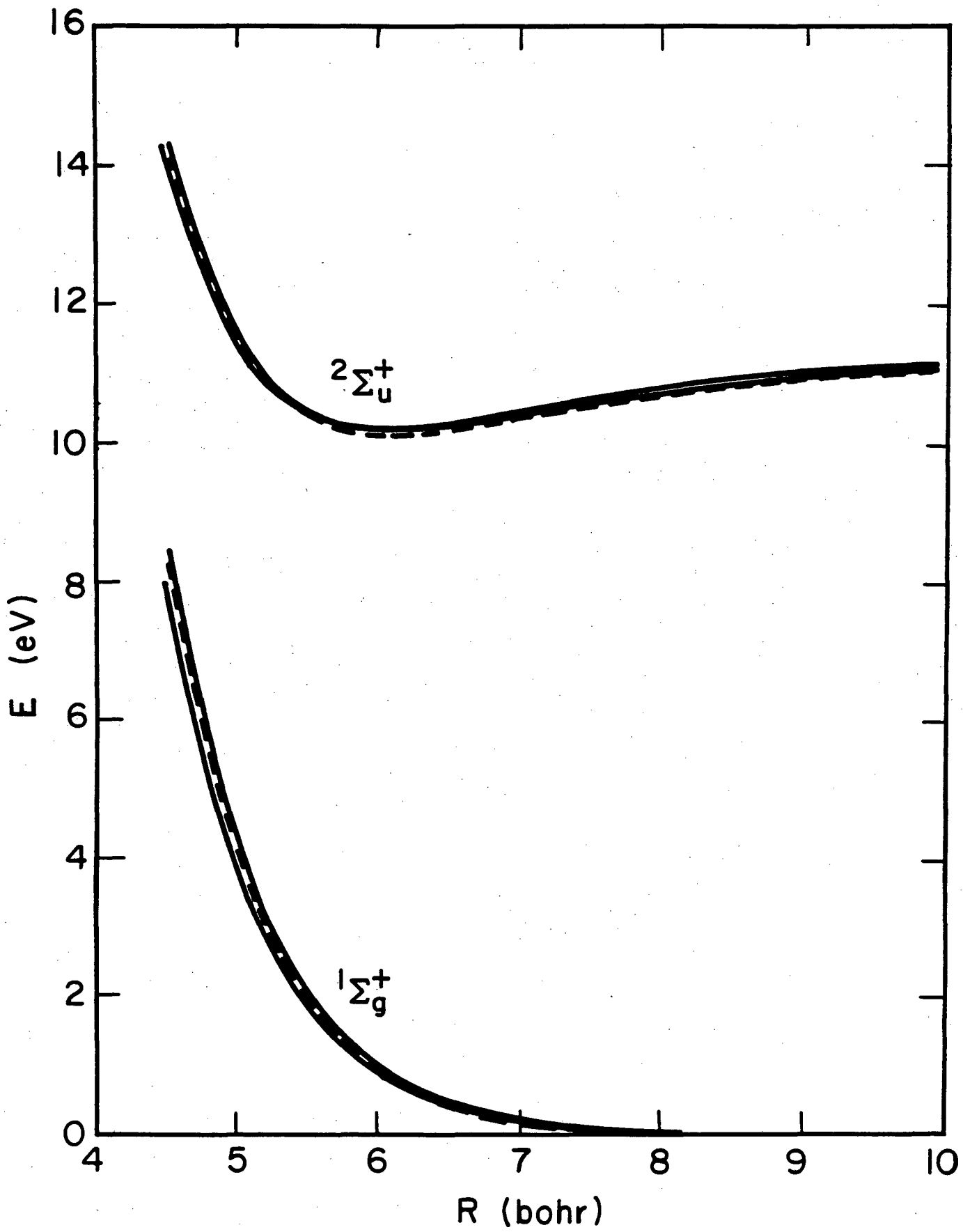
Figure Captions

1. Comparison of AE and EP dissociation curves for Ar_2 and Ar_2^+ from POL CI calculations (dashed lines from Ref 11, solid lines from this work).
2. Comparison of AE, EP and AREP dissociation curves for Kr_2 and Kr_2^+ from POL CI calculations (dashed lines from Ref 11, solid lines from this work with AREP less repulsive than EP).
3. Comparison of AE, EP and AREP dissociation curves for Xe_2 and Xe_2^+ from POL CI calculations (dashed lines from Ref 11, solid lines from this work with AREP less repulsive than EP).
4. Comparison of present EP and AREP dissociation curves for Xe_2 with AE curves, EP and REP curves from Ref 15 and with AREP curves from Ref 16.
5. Comparison of present EP and AREP dissociation curves for Xe_2^+ with AE curves, EP and REP curves from Ref 15 and with AREP curves from Ref 16.
6. Xe_2^+ dissociation curves (including semiempirical spin-orbit correction) for $\text{I } (1/2)_u$, $\text{II } (1/2)_u$ and $(3/2)_u$ states. Curves were computed using the present AREPs and are compared with AE curves from Ref 15.

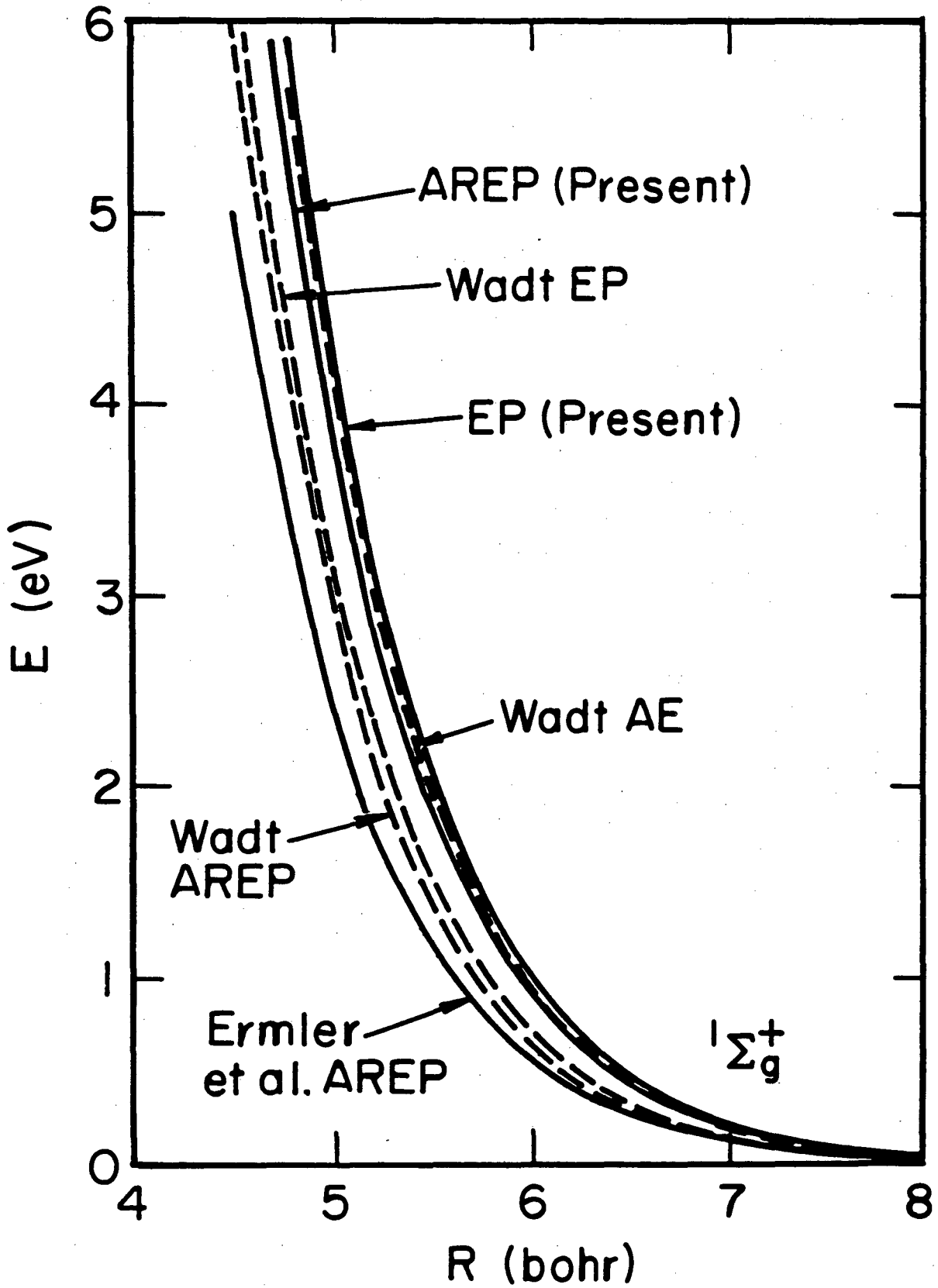


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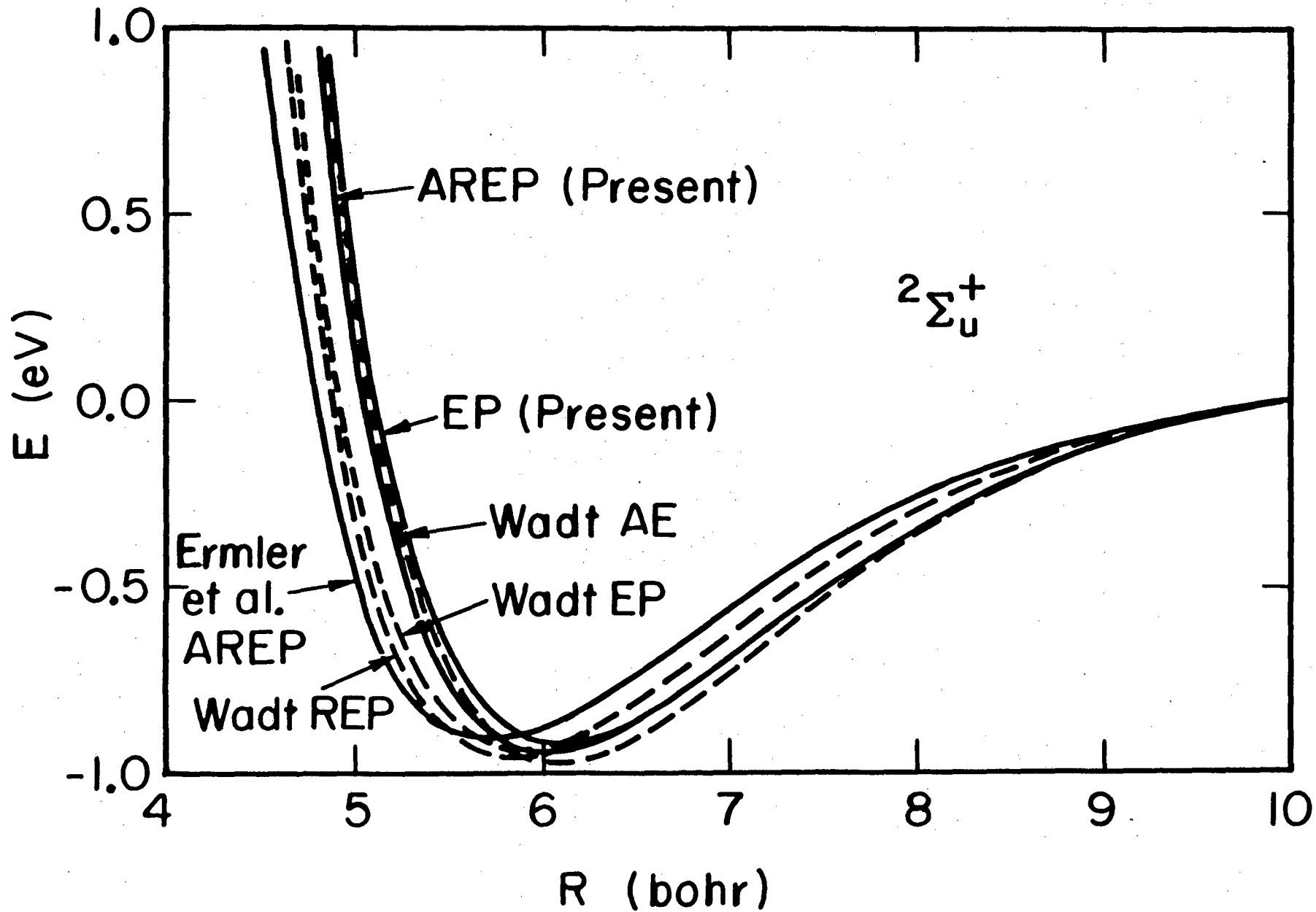




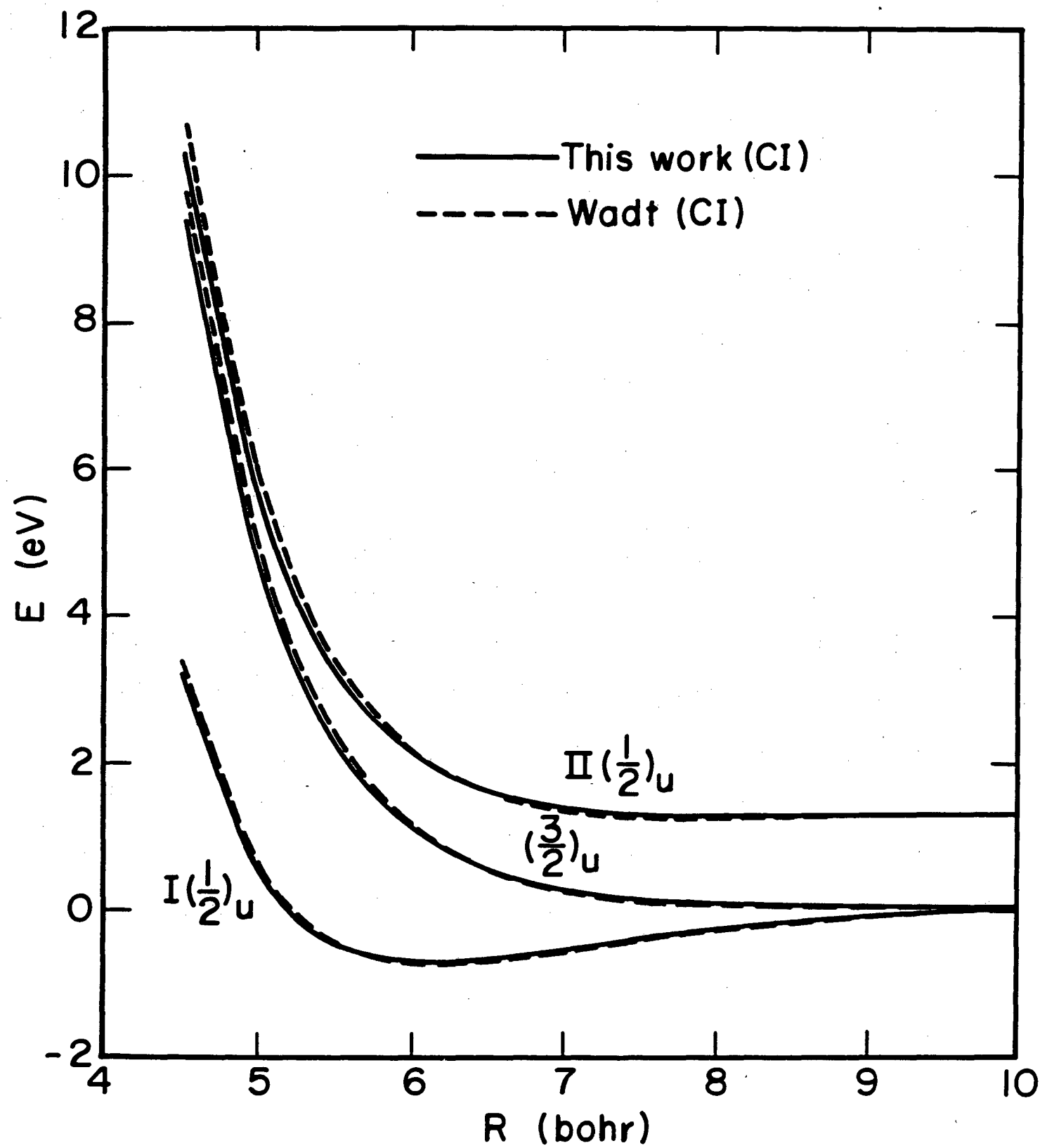
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