

## Extended model potential calculations on I<sub>2</sub> and HI molecules

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In systems with large core–valence exchange interactions, it is difficult to reproduce the results of all-electron (AE) SCF calculations by using effective core potential methods. Unfortunately, this difficulty is often found just where the valence–electron methods are expected to be most advantageous: in calculations on molecules containing heavier atoms. In the model potential (MP) method of Sakai and Huzinaga,<sup>1</sup> these difficulties may be overcome by using adjustable (“soft”) values of the core projector parameters<sup>2</sup> and/or by promoting the outermost core orbitals into the valence space. The promoted electrons are then treated either via the frozen-orbital technique<sup>3</sup> or by explicitly merging them with the valence electrons.<sup>2,4</sup> The latter approach was also recommended<sup>5</sup> as a means to improve results of the effective core potential method.<sup>5</sup>

Recently, the MP method has been improved by inclusion of the nonlocal approximation to the core–valence exchange terms.<sup>6</sup> This extended model potential (EMP) method was applied in calculations on ScO. Even though the ScO molecule is a difficult test case for effective core potential techniques, the EMP method dealt with it successfully. Here, we illustrate the efficiency of the EMP method in the treatment of such difficult cases by applying it to studies on I<sub>2</sub> and HI. I<sub>2</sub> is known to be a difficult target for effective core potential methods. The difficulties, whose origin was analyzed by Strømberg *et al.*,<sup>3</sup> are successfully overcome by the EMP method.

The (8|6|8) valence basis set for iodine used to expand the 5s and 5p orbitals (in the 5s<sup>2</sup>5p<sup>5</sup>–<sup>2</sup>P ground state) and the 5s, 5p, and 5d orbitals (in the 5s<sup>2</sup>5p<sup>4</sup>5d<sup>1</sup>–<sup>4</sup>F state), was obtained as proposed by Klobukowski.<sup>4</sup> The reference 5s and 5p orbitals were taken from the atomic calculation on I(<sup>2</sup>P) using (43333|4333|43) basis set.<sup>7</sup> The reference 5d orbital was the numerical Hartree–Fock (HF) orbital of the 5s<sup>2</sup>5p<sup>4</sup>5d<sup>1</sup>–<sup>4</sup>F state. This (8|6|8) basis set was used in the nonlocal expansion of the total (inner and outer) core–valence exchange operator.<sup>6</sup> The inner-core (1s2s2p3s3p3d) and outer-core (4s4p4d) Coulomb potentials were expanded in terms of 1s GTFs.<sup>6</sup> The orbital energies in both <sup>2</sup>P and <sup>4</sup>F states and the transition energy <sup>2</sup>P→<sup>4</sup>F (Table I) illustrate the quality of the EMP obtained. The transferability of the

EMP optimized in the ground state to the excited <sup>4</sup>F state is very satisfactory.

In the molecular calculations with 5s and 5p valence orbitals (EMP in Table II) the basis set was contracted as [5|4|1\*]. This contraction releases the GTFs which are more important in the description of the outermost region of the 5s and 5p orbitals. Standard d-type polarization function<sup>7</sup> was used. The five term basis set for hydrogen<sup>8</sup> was contracted to (41), scaled by a factor of 1.2, and augmented by one p-type polarization function (exponent = 0.48).

The EMP results for the ground state of I<sub>2</sub> and HI are shown in Table II together with the near HF,<sup>9</sup> reference AE, other effective core potentials,<sup>2,3</sup> and experimental values.<sup>10</sup> The EMP results differ from the reference AE values by approximately 0.04–0.02 Å in the equilibrium distance, R<sub>e</sub>, 3%–2% in the vibrational frequency ω<sub>e</sub>, 0.4 eV in the binding energy D<sub>e</sub>, and 10<sup>–3</sup> a.u. in the molecular orbital energies ε. The EMP results obtained with uncontracted basis for I<sub>2</sub> and HI show a notable improvement of the D<sub>e</sub> value and negligible change of R<sub>e</sub> and ω<sub>e</sub>. As shown in Table II, the CPU time of the EMP calculations is significantly smaller than the time needed for the AE calculations.

The comparison of our SCF results for I<sub>2</sub> with results from previous calculations is very encouraging. In the calculation by Strømberg *et al.*<sup>3</sup> all core orbitals up to 3d were represented by a Huzinaga-type model potential; the outer-core (4s4p4d) orbitals, represented by a truncated basis set, were included in the valence space and were kept frozen. This frozen-orbital technique of handling the valence–outer core interactions is obviously more computer-time consuming than the EMP method, while the quality of results is similar: the present R<sub>e</sub> value differs by only 0.01 Å from the one of Strømberg *et al.*,<sup>3</sup> and our ω<sub>e</sub> value is closer to the AE one.

We can also compare our EMP results with the ones from MP calculations.<sup>2</sup> Our SP valence calculation leads to results which are closer to the AE values than the ones from the comparable MP SP calculation.<sup>2</sup> This comparison shows the importance of the nonlocal representation of the exchange terms. It should be noted that the values of the projection parameters, B<sub>k</sub>'s were fixed at the recommended

TABLE I. Atomic results.

	5s <sup>2</sup> 5p <sup>5</sup> – <sup>2</sup> P		5s <sup>2</sup> 5p <sup>4</sup> 5d <sup>1</sup> – <sup>4</sup> F			<sup>2</sup> P→ <sup>4</sup> F/cm <sup>–1</sup>
	ε(5s)	ε(5p)	ε(5s)	ε(5p)	ε(5d)	
EMP	–0.815 70	–0.401 75	–0.946 96	–0.560 03	–0.070 61	62 150
Reference AE <sup>a</sup>	–0.819 05	–0.401 75	–0.942 28	–0.552 06	–0.071 10	62 269

<sup>a</sup> 5s<sup>2</sup>5p<sup>5</sup>–<sup>2</sup>p: (43333|4333|43) from Ref. 7; 5s<sup>2</sup>5p<sup>4</sup>5d<sup>1</sup>–<sup>4</sup>F: basis set from Ref. 7; (433321|43321|4211\*) plus three additional d GTO. Orbital energies in atomic units.

TABLE II. Molecular results for I<sub>2</sub> and HI.

I <sub>2</sub>	R <sub>e</sub> /Å	ω <sub>e</sub> /cm <sup>-1</sup>	D <sub>e</sub> /eV	Integ.	Timing/s <sup>a</sup> SCF/Iter.	Total
Exptl. (Ref. 10)	2.667	214.5	1.56			
Near HF <sup>b</sup>	2.678	241	0.96			
Reference AE <sup>c</sup>	2.700	241	0.84	1440	44.5	2514
EMP	2.739	233	0.40	51	2.2	41
Uncontracted EMP	2.740	232	0.56	90	7.2	241
Reference 3	2.728	222				
(5s5p) SP (Ref. 2)	2.757	226				
(4d 5s5p) DSP (Ref. 2)	2.732	227				
	1σ <sub>g</sub>	1σ <sub>u</sub>	2σ <sub>g</sub>	1π <sub>u</sub>	1π <sub>g</sub>	2σ <sub>u</sub> <sup>e</sup>
ε(EMP) - ε(AE) <sup>d</sup>	0.002 08	-0.005 26	0.005 46	-0.000 49	-0.004 88	0.005 07
HI	R <sub>e</sub> /Å	ω <sub>e</sub> /cm <sup>-1</sup>	D <sub>e</sub> /eV	Integ.	Timing/s <sup>a</sup> SCF/iter.	Total
Exptl. (Ref. 10)	1.61		3.21			
Reference AE <sup>c</sup>	1.620	2474	2.46	317	3.4	402
EMP	1.636	2415	2.09	16	0.5	28
Uncontracted EMP	1.635	2433	2.17	39	1.7	80
	1σ	2σ	1π	3σ <sup>f</sup>		
ε(EMP)-ε(AE) <sup>f</sup>	0.003 07	0.004 51	0.000 29	0.026 38		

<sup>a</sup>The tabulated times correspond to one I-I or H-I distance. The calculations were done in an AMDAHL 580/FF using a modified version of Almlöf's MOLECULE (Ref. 12).

<sup>b</sup>These calculations include *f*-type polarization functions (Ref. 9).

<sup>c</sup>I-(433321|43321|4211\*) from Ref. 7; H-(4|1|1\*) from Ref. 8 (*p* exponent = 0.48).

<sup>d</sup>*r*(I-I) = 5.0 a.u.

<sup>e</sup>First virtual orbital.

<sup>f</sup>*r*(I-H) = 3.0 a.u.

-2ε<sub>k</sub>,<sup>11</sup> while in the MP SP calculations they were treated as adjustable parameters. Furthermore, our SP results and the MP DSP (4*d* treated explicitly) results are of a comparable quality.

The same situation was observed in ScO.<sup>6</sup> Therefore, in systems with large core-valence exchange interactions, it seems that the EMP method with nonlocal potential, which explicitly involves only the valence electrons and uses the fixed projection operator parameters, can reproduce the AE SCF calculations with the same degree of accuracy which in the previous MP treatment may be achieved only when the outermost core orbital is promoted to the valence space and the core-projector parameters are optimized.

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