The *ab initio* model potential method. Main group elements

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In this paper we present the *ab initio* core model potential method, in which the Coulomb and exchange core operators J_c and K_c are represented as accurately as possible using adequate local and nonlocal potentials, and the valence basis set is optimized in atomic MP SCF calculations following the variational principle. Nonrelativistic model potential parameters and valence basis sets are presented for the main group elements from Li to Xe. The pilot SCF molecular calculations on the ground states of N_2, P_2, As_2, Sb_2, and CaO show a good agreement between all-electron and model potential results, in particular the changes observed in molecular results due to improvements of the valence part of the all-electron basis set are reproduced by the model potential calculations.

I. INTRODUCTION

The chemical ideas about the formation of molecules are the basis of the valence-electron methods; their main goal is to make feasible calculations that would be prohibitively expensive at the all-electron (AE) level, without appreciable loss of accuracy if the same kind of wave function and valence basis set is used.

A number of different valence-electron methods have been proposed in recent years (see, e.g., Refs. 1, 2, and references therein) and extensive tabulations of parameters have been published.[3,4] The one-electron effective potentials are generally obtained in atomic calculations oriented to the reproduction of the AE valence atomic orbital energies and shapes, and they frequently lead to acceptable molecular results if the core and valence orbitals are clearly separated.

Among the valence-electron methods, the model potential (MP) method[5] is the only one that makes use of valence orbitals showing the correct nodal structure. The formalism is based on the theory of separability of many electron systems in which strong orthogonality among subsystem wave functions is assumed while evaluating the system total energy,[6,7] and from which the form of the one-electron effective Hamiltonian emerges naturally. Different approximations to this operator lead to the various versions of the model potential method. After the first proposal[5] and later improvements[8] the method produced good molecular results,[2] the only exception being cases for which core and valence orbitals of the same atom are close in energy and shape (e.g., ScO, I_2). A very careful analysis, reported by Petterson and Strömberg,[9] showed that the difficulties encountered in these cases stemmed from the wrong long-range behavior of the local potentials, resulting from the accommodation of the strong nonlocal exchange interactions between valence and outer-core orbitals in the atomic optimization; at the same time, the good results produced by a frozen-core approach ruled out the occurrence of core polarization.[10] These problems were solved after the use of a nonlocal operator to represent the outer-core valence exchange interactions, together with the atomic optimization of only the inner-core local potentials.[11]

A new version of the model potential method is presented here which keeps the virtues of the latest one[11] and is based on an *ab initio* philosophy. In this method, the attention is not focused on the reproduction of the valence atomic orbital energies and shapes but on the correct representation, by adequate potentials, of the Coulomb and exchange core operators J_c and K_c which depend only on the core orbitals. A local potential is used to represent J_c, whereas K_c is represented by a nonlocal potential that guarantees the exact calculation of all the one-center integrals involving K_c and the valence basis set functions. The parameters of the representations of J_c and K_c are thus obtained for a particular atom according to the criterion of quality expressed above. Then, since J_c and K_c describe physical interactions, their representation is not changed anymore; instead, the optimization of the atomic valence basis set is performed by minimization of the valence energy. In this way, the atomic model potential problem becomes entirely equivalent to the one of optimization of all-electron basis sets.

In atomic calculations, this method is equivalent to the frozen-core limit, provided the local representation of J_c is good enough; therefore, even if nothing is explicitly done in order to reproduce AE atomic orbital energies and shapes, the MP ones are close to them, the better the basis set the closer. In molecular calculations, the *ab initio* model potential method is as close to the frozen-core limit as the many-center core–valence exchange integrals are unimportant. In cases for which such integrals are relevant to the molecular results, the frozen-core limit itself might be doubtful and the corresponding core orbitals might have to be promoted to the valence space.

In this paper we present the details of the method (Sec. II) as well as the model potentials and valence basis sets for the main group elements (Sec. III). The results of SCF pilot molecular calculations on N_2, P_2, As_2, and Sb_2, as well as on CaO, are reported in Sec. IV. These calculations show that the AE and MP results obtained with equivalent valence basis sets are close, and that the changes observed in molecular results due to improvements of the valence part of the AE basis set are reproduced by the MP calculations.

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II. METHOD

A. Atomic formalism

The nonrelativistic MP Hamiltonian for the N valence electrons of an atom may be written in atomic units as[6]

$$H(1,2,...,N) = \sum_{i=1}^{N} h(i) + \sum_{i>j}^{N} r_{ij}^{-1} , \qquad (1)$$

where the one electron Hamiltonian $h(i)$ may be expressed as

$$h(i) = -\tfrac{1}{2}\Delta_i - (Z - Z_{\text{core}})/r_i$$
$$+ V_{\text{Coul}}(i) + V_{\text{exch}}(i) + P(i) . \qquad (2)$$

In Eq. (2), the first two terms represent the kinetic energy and the attraction of the nucleus whose charge Z is completely shielded by the Z_{core} electrons. The projector $P(i)$,

$$P(i) = -\sum_c^{\text{core}} 2\epsilon_c |\phi_c\rangle\langle\phi_c| , \qquad (3)$$

constructed using the core orbital energies (ϵ_c) and functions (ϕ_c), prevents the valence orbitals from collapsing onto the core space. $V_{\text{Coul}}(i)$ includes the core Coulomb operators, J_c, and is a local radial operator,

$$V_{\text{Coul}}(i) = V_{\text{Coul}}(r_i) = -Z_{\text{core}}/r_i + 2\sum_c^{\text{core}} J_c(i) . \qquad (4)$$

Finally, $V_{\text{exch}}(i)$ represents the nonlocal core exchange operator,

$$V_{\text{exch}}(i) = -\sum_c^{\text{core}} K_c(i) . \qquad (5)$$

In order to reduce the computing time in molecular calculations, further simplifications of Eqs. (4) and (5) are needed. The local Coulomb potential is approximated as in Ref. 8:

$$V_{\text{Coul}}(r_i) \simeq V_{\text{Coul}}^{\text{MP}}(r_i) = \sum_k A_k r_i^{n_k} \exp(-\alpha_k r_i^2)/r_i ,$$
$$(6)$$

where the parameters $\{A_k, \alpha_k\}$ are determined through least-square fitting to the potential $V_{\text{Coul}}(r_i)$ calculated with Eq. (4) using AE core orbitals. A nonlocal representation is used for the exchange potential in Eq. (5) (this representation[12] was already used in Ref. 11 for the exchange potential associated with the outermost core orbitals only),

$$V_{\text{exch}}(i) \simeq V_{\text{exch}}^{\text{MP}}(i) = \sum_l \sum_{m=-l}^{l} \sum_{a,b} |alm\rangle A_{l;ab} \langle blm| ,$$
$$(7)$$

where the $\{|alm\rangle\}$ are products of radial primitive Gaussian-type functions and spherical harmonics, and the coefficients $A_{l;ab}$ are the elements of the matrix

$$A = S^{-1}KS^{-1} , \qquad (8)$$

where

$$S_{ij} = \langle i|j\rangle, \quad K_{ij} = \langle i|V_{\text{exch}}|j\rangle , \qquad (9)$$

$|i\rangle, |j\rangle$ being functions of the set $\{|alm\rangle\}$. This implies that if all the valence primitive functions are contained in the set $\{|alm\rangle\}$, then

$$\langle i|V_{\text{exch}}^{\text{MP}}|j\rangle = \langle i|V_{\text{exch}}|j\rangle , \qquad (10)$$

and, in atoms, the same result is obtained by the use of V_{exch} [Eq. (5)] or $V_{\text{exch}}^{\text{MP}}$ [Eq. (7)].

Once an atomic AE SCF calculation is done and a core-valence partition is chosen, the atomic core orbitals are used to obtain the operators P, $V_{\text{Coul}}^{\text{MP}}$, and V_{exch} as indicated. These operators are not changed anymore. The valence basis set is then optimized by minimization of the valence SCF energy using standard AE methods.[13]

B. Molecular formalism

The nonrelativistic MP Hamiltonian for the N valence electrons of the molecule may be written in atomic units as[5]

$$H(1,2,...,N) = \sum_{i=1}^{N} h(i) + \sum_{i>j}^{N} r_{ij}^{-1} + \sum_{I>J} V_{IJ}(R_{IJ}) ,$$
$$(11)$$

where (i,j) run over electrons, (I, J) run over nuclei, the one-electron Hamiltonian can be expressed as

$$h(i) = -\tfrac{1}{2}\Delta_i - \sum_I (Z^I - Z_{\text{core}}^I)/r_{Ii}$$
$$+ \sum_I [V_{\text{Coul}}^I(i) + V_{\text{exch}}^I(i) + P^I(i)] , \qquad (12)$$

and the internuclear repulsion is approximated by

$$V_{IJ}(R_{IJ}) = (Z^I - Z_{\text{core}}^I)(Z^J - Z_{\text{core}}^J)/R_{IJ} . \qquad (13)$$

The last term of Eq. (12) collects the sum of all effective core potential contributions. For each center I, Eqs. (3), (6), and (7) are used.

The basis set used for the MP molecular calculation is formed by the atomic valence basis sets augmented with the same extra functions that would be necessary for an AE molecular calculation, such as polarization functions, diffuse functions, etc. It is important to notice that the whole set of primitives used in the MP molecular basis set on a particular center must be used to obtain $V_{\text{exch}}^{\text{MP}}$ through Eqs. (7)–(9); only then the one-center integrals fulfill Eq. (10). There is no guarantee of a good reproduction of the many-center integrals $\langle i|V_{\text{exch}}|j\rangle$ within this method, but these integrals are expected to have a minor influence in the molecular results if the core approximation is acceptable.

III. MODEL POTENTIALS AND BASIS SETS

In this section we present the model potential parameters for the main group elements up to $Xe(Z = 54)$, as well as the valence Gaussian basis sets. All of them were obtained for the atomic ground states.

To generate the core potentials we have used *well-tempered* (WT) core orbital functions and energies,[14] whose quality is very close to the HF limit. The local Coulomb model potential parameters [Eq. (6)], obtained through least-square fitting to the reference V_{Coul} [Eq. (4)], appear in Table I. The parameters $A_{l;ab}$ of the exchange model potential, $V_{\text{exch}}^{\text{MP}}$, can be easily and cheaply calculated using Eqs. (8) and (9), once the core orbitals and the basis set on a given center are known; besides, addition of extra functions to the molecular basis set results in a change of the matrix A, making a tabulation of these coefficients useless. Neverthe-

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TABLE I. Local Coulomb model potential parameters [Eq. (6)] for the main group elements.

(A) Li to Ne

	Lithium		Beryllium		Boron		Carbon
α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$
197775.87	0.012 836 59	220020.68	0.016 393 47	215139.23	0.021 150 97	233033.66	0.024 256 10
17359.376	0.023 658 82	20793.906	0.028 679 84	19835.800	0.037 816 90	22911.775	0.041 566 23
2589.8142	0.052 932 29	3317.9723	0.061 783 98	3054.8389	0.084 178 88	3674.7801	0.091 465 26
479.85840	0.113 405 28	665.20534	0.124 719 55	575.05226	0.183 080 32	709.91865	0.198 155 16
100.99238	0.243 128 08	156.80300	0.248 982 78	120.79038	0.415 346 87	152.64877	0.444 270 02
23.344189	0.524 191 86	40.276502	0.514 595 79	27.817362	0.800 857 12	36.739553	0.793 055 16
6.0313748	0.766 184 49	11.365749	0.728 011 05	7.4285524	0.457 568 95	10.405237	0.407 232 08
1.8247933	0.263 662 59	3.6518552	0.276 833 53				

	Nitrogen		Oxygen		Fluorine		Neon
α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$
249574.95	0.027 168 37	265207.54	0.029 916 19	279347.40	0.032 583 07	292201.25	0.035 187 86
25950.235	0.044 828 97	28994.950	0.047 680 30	31889.749	0.050 377 72	34636.084	0.052 966 94
4316.5926	0.097 594 36	4987.8146	0.102 752 95	5649.9776	0.107 598 81	6298.7650	0.112 237 28
854.52037	0.210 399 64	1010.7038	0.220 273 81	1169.2730	0.229 403 30	1328.7256	0.238 043 60
188.10814	0.465 126 13	227.61180	0.480 038 24	269.05132	0.492 686 20	311.99355	0.503 870 35
46.985771	0.782 647 08	58.649698	0.771 869 95	71.298846	0.760 786 65	84.793581	0.749 843 04
13.841363	0.372 235 45	17.774210	0.347 468 56	22.121507	0.326 564 25	26.839989	0.307 850 93

(B) Na to Ar

	Sodium		Magnesium		Aluminum		Silicon
α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$
306276.69	0.061 697 72	322460.63	0.066 357 06	322316.36	0.073 232 55	321661.05	0.079 730 64
40442.846	0.083 732 52	43150.295	0.091 508 33	42989.923	0.100 214 99	43207.704	0.110 086 51
7853.4833	0.181 456 49	8125.2571	0.199 476 90	8384.6495	0.213 505 90	8274.9011	0.236 222 51
1617.2936	0.396 248 97	1723.2683	0.424 970 75	1758.5767	0.467 256 57	1749.9335	0.508 534 02
358.08855	0.867 352 43	364.94933	0.997 987 18	391.23867	1.015 371 50	400.57869	1.067 963 60
83.017333	1.510 495 50	86.582869	1.458 908 00	94.113283	1.524 382 80	99.579081	1.521 547 30
16.062158	1.815 883 40	17.842786	1.960 104 50	19.503874	2.019 059 80	21.081645	2.141 245 20
4.1341426	3.620 645 90	4.9130123	3.550 096 40	5.8771986	3.479 318 70	6.7885626	3.383 845 80
1.3070163	1.462 487 10	1.7232380	1.250 590 90	2.1757348	1.107 657 10	2.6333940	0.950 824 48

	Phosphorus		Sulfur		Chlorine		Argon
α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$
325164.01	0.086 677 05	324985.01	0.093 359 33	310528.24	0.103 886 11	337361.63	0.104 026 63
42054.732	0.122 563 42	42169.635	0.131 821 93	38001.960	0.150 502 57	45322.027	0.141 999 65
8085.0454	0.256 618 36	8071.8331	0.278 778 90	7723.3953	0.283 947 85	9124.5281	0.291 313 86
1749.5593	0.545 621 13	1736.8547	0.593 543 54	1824.0639	0.602 477 50	2028.8217	0.621 714 39
409.85995	1.123 832 50	412.56100	1.177 697 20	437.69730	1.237 322 40	492.09122	1.206 704 70
104.50231	1.505 127 90	108.42851	1.478 066 50	110.70253	1.535 358 60	131.95021	1.484 577 10
22.907208	2.257 264 40	24.540590	2.419 414 30	25.121295	2.617 702 10	30.190174	2.631 432 70
7.7043508	3.307 861 30	8.5385050	3.163 021 90	9.3089863	2.918 010 70	10.475381	3.154 134 70
3.0905313	0.794 434 02	3.6014875	0.664 296 38	4.0576817	0.550 792 10	4.1630541	0.364 096 28

(C) K to Kr

	Potassium		Calcium		Gallium		Germanium
α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$
461901.07	0.098 059 69	466371.83	0.103 621 10	604373.01	0.164 530 66	668170.88	0.164 007 89
86512.061	0.099 772 37	88304.012	0.103 214 17	116902.66	0.175 187 24	124788.59	0.181 126 44
22412.605	0.187 597 17	24324.885	0.181 117 18	28184.217	0.353 946 86	28572.403	0.383 706 92
6189.4394	0.344 223 73	7057.1830	0.336 668 58	6958.4486	0.728 186 03	6629.5546	0.799 476 20
1804.9293	0.654 303 07	2091.6860	0.643 212 95	1753.3081	1.459 814 80	1705.6954	1.456 149 30
527.85264	1.248 450 80	590.11433	1.341 471 50	492.01373	1.939 833 30	512.86719	1.890 988 70

TABLE I. (*continued*).

Potassium		Calcium		Gallium		Germanium	
α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$
148.35180	1.732 648 40	149.62063	1.895 202 90	138.21712	2.983 322 90	144.57550	3.129 322 10
34.483334	3.169 014 40	33.796219	3.628 127 30	47.039636	5.318 371 30	48.966203	5.298 731 80
12.519648	3.537 096 70	12.131936	3.333 534 50	10.176595	5.383 841 60	10.877774	5.385 942 10
4.7156102	0.834 954 72	2.4212416	1.183 723 00	3.6465148	7.962 867 70	4.0462753	7.978 742 40
1.5557737	4.001 572 40	1.8637404	3.200 855 90	1.1349591	1.530 097 60	1.3237059	1.331 806 20
0.62020299	2.092 306 40	0.78607810	2.049 250 90				

Arsenic		Selenium		Bromine		Krypton	
α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$
484958.78	0.203 318 87	457507.75	0.220 005 91	409488.26	0.246 194 73	400264.05	0.258 873 20
88634.843	0.217 638 19	80031.950	0.241 104 58	66039.300	0.284 497 40	62772.198	0.310 170 71
22298.484	0.411 040 53	20352.326	0.435 342 17	17121.854	0.461 517 01	15453.661	0.525 635 13
6024.8223	0.785 650 53	5740.5503	0.813 618 54	5324.0861	0.826 720 60	4780.7699	0.873 121 96
1736.5054	1.416 191 40	1698.7633	1.456 876 10	1638.3064	1.506 864 70	1557.9845	1.518 984 00
532.24528	1.947 389 30	528.71695	1.950 468 10	515.63444	1.953 924 20	501.26828	1.972 587 00
146.80340	3.281 022 10	149.05323	3.375 936 60	150.32257	3.445 047 20	150.23603	3.525 551 50
50.827620	5.205 155 80	52.905476	5.109 993 80	55.211961	4.983 907 70	57.491638	4.809 253 30
4.4870079	7.714 615 90	12.137970	5.545 431 10	12.843973	5.698 372 60	13.652700	5.825 130 40
1.6008273	1.308 118 60	4.9826357	7.558 574 60	5.4121554	7.415 471 10	5.8599548	7.316 253 20
11.429694	5.509 858 60	1.8803067	1.292 648 40	2.1081169	1.177 482 80	2.3357475	1.064 439 60

(D) Rb to Xe

Rubidium		Strontium		Indium		Tin	
α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$
523013.83	0.229 449 79	508525.56	0.241 907 84	513078.50	0.339 404 12	505885.29	0.351 436 18
101467.04	0.232 130 18	96664.694	0.249 306 17	96872.828	0.359 102 71	94758.301	0.373 407 44
26873.082	0.432 354 24	25412.882	0.457 875 03	24538.182	0.694 653 03	24056.555	0.717 464 93
7365.8358	0.854 161 79	7194.2830	0.859 251 53	6507.0196	1.369 458 60	6440.9793	1.397 898 00
2012.2435	1.664 170 20	2087.5397	1.615 535 90	1802.7142	2.286 103 70	1817.2952	2.282 249 50
561.27580	2.275 002 80	600.99832	2.289 280 30	477.95667	3.390 657 30	488.95799	3.418 686 00
150.16189	4.276 323 10	156.77367	4.488 770 00	147.82476	6.559 554 50	153.17053	6.555 923 60
53.368312	4.985 052 10	54.438184	4.957 663 90	35.948271	6.713 001 20	37.228099	6.883 442 10
11.711820	9.246 370 60	12.292335	9.378 866 50	16.504596	9.358 218 40	17.401815	9.155 809 90
4.7534243	5.317 445 00	5.3635348	4.758 577 80	3.2479844	7.414 761 00	3.4506948	7.294 935 70
1.0302226	4.814 682 90	1.3343487	4.384 641 50	1.7040402	6.046 540 50	1.9822675	5.912 106 10
0.42157436	1.672 857 30	0.58740385	2.318 323 70	0.69440997	1.468 545 00	0.85527098	1.656 640 40

| Antimony		Tellurium		Iodine		Xenon	
α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$
497609.59	0.363 956 54	505679.94	0.369 105 73	503638.22	0.378 205 73	506699.42	0.385 439 98
92504.954	0.389 081 78	94240.376	0.395 493 89	94486.865	0.401 929 61	95214.925	0.409 312 13
23373.187	0.749 761 36	23790.911	0.760 376 50	24039.834	0.771 735 23	24338.287	0.780 638 53
6261.5981	1.446 535 60	6415.7044	1.452 834 50	6514.7999	1.469 384 60	6666.5180	1.471 499 90
1785.5062	2.310 240 70	1847.2904	2.307 155 60	1889.9015	2.310 904 70	1955.7125	2.307 310 80
480.11923	3.555 324 00	501.38363	3.548 815 40	516.31914	3.576 853 50	536.29236	3.599 428 40
154.35927	6.461 884 40	161.65705	6.486 983 70	167.57843	6.483 560 50	174.21287	6.499 984 10
38.309384	6.894 720 80	40.223229	6.884 424 90	42.030271	6.868 682 00	43.794882	6.889 691 10
18.399413	9.040 555 70	19.642565	8.986 783 00	20.840443	8.947 328 20	22.096924	8.861 437 20
3.5915358	6.950 304 00	3.8624144	7.216 979 40	4.0879536	7.324 756 70	4.3327711	7.460 388 70
2.4609435	5.519 713 60	2.5951516	5.580 026 30	2.8218398	5.602 867 00	3.0505983	5.616 584 70
1.0924944	2.317 921 50	1.1879745	2.011 021 20	1.2985977	1.863 792 20	1.4058161	1.718 284 40

All the exponents n_k [Eq. (6)] are set to 0.
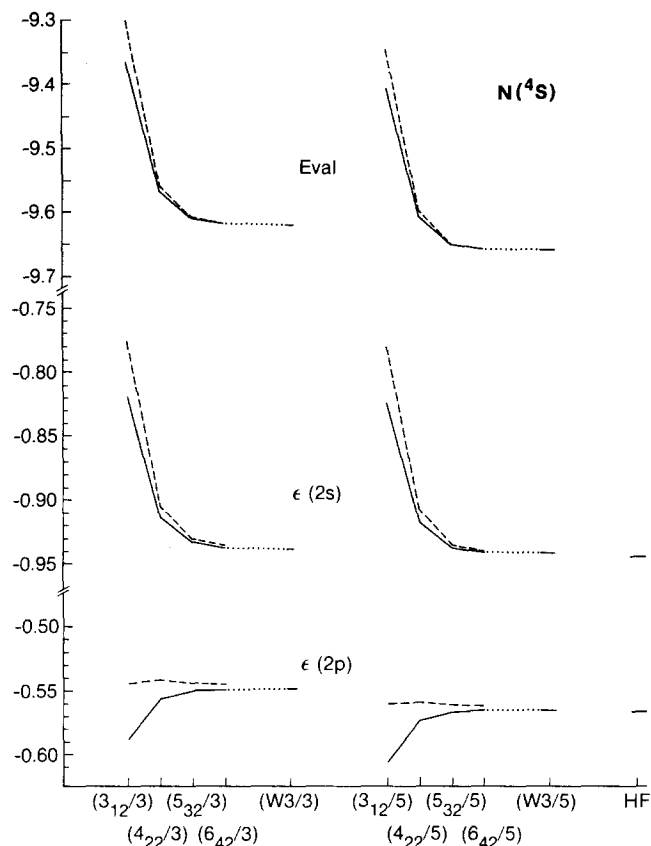
FIG. 1. Valence and orbital energies for N(^4S), in a.u. Solid line: completely optimized valence basis set; dashed line: only the innermost primitives were optimized.
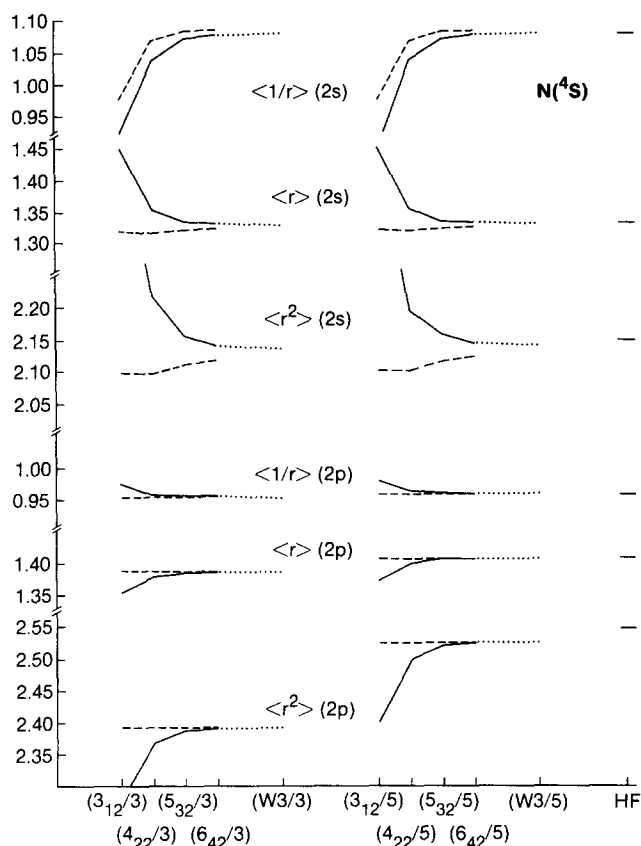

FIG. 2. Radial expectation values for the valence orbitals of N(^4S) in a.u. Solid line: completely optimized valence basis set; dashed line: only the innermost primitives were optimized.

less, they can be obtained from the authors upon request. The calculation of these parameters can be a part of the input processing during the molecular calculation.

In order to decide upon the adequate size and pattern for the valence basis sets, a series of exploratory calculations were done. In Figs. 1 and 2 we present the valence orbital energies and radial expectation values, as well as the valence energy, for N(^4S) using basis sets $(n_{n-2,2}/3)$ and $(n_{n-2,2}/5)$, with $n = 3, 4, 5,$ and 6; the HF results[15] are also presented. Here we use the notation of Ref. 13 for contracted basis sets and add some subindexes in order to show the structure of signs in the contraction coefficients. For instance, $(5_{32}/3)$ means that the coefficients of the three innermost s-type primitives have opposite sign to those of the two outermost ones. This implies tht only the last two functions represent the main regions of the $2s$ orbital, whereas the first three mainly provide the ability to reach $1s$–$2s$ orthogonality.

It can be observed in Figs. 1 and 2 that the results of the completely optimized basis sets (solid line) converge to the corresponding MP($W3_{12}/3$) and MP($W3_{12}/5$) values. These last basis sets were constructed using the 14-primitive $1s$ WT orbital[14] (symbolized by W) as an inner contracted function to ensure that the $2s$ orbital has full ability to be orthogonal to the $1s$ core orbital, and the rest of the basis set was optimized along AE($W3/3$) and AE($W3/5$) calcula-
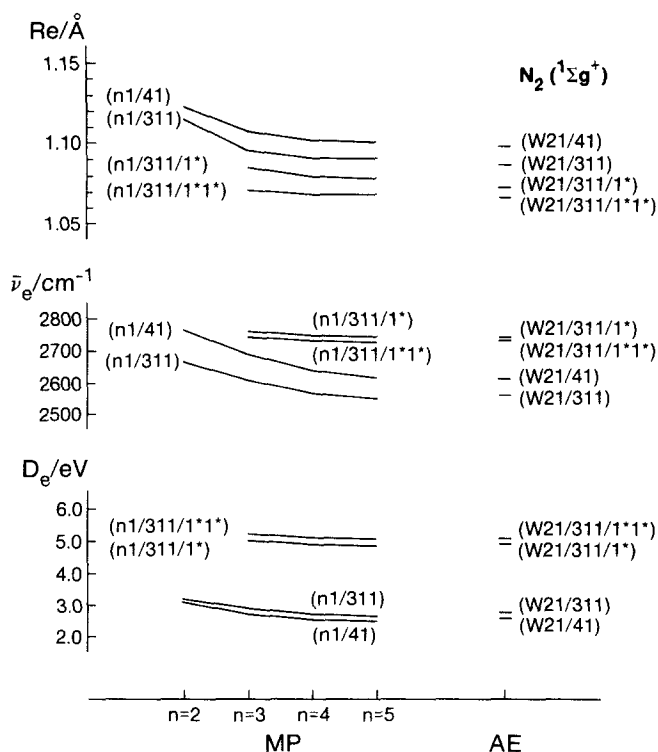

FIG. 3. MP and AE molecular results on $N_2(^1\Sigma_g^+)$.

TABLE II. MP basis sets.

(A) IA–IIA group

Lithium		Beryllium		Sodium		Magnesium	
Exp.	Coeff.	Exp.	Coeff.	Exp.	Coeff.	Exp.	Coeff.
$2s$		$2s$		$3s$		$3s$	
30.381413	− 0.013 572 91	65.231845	− 0.013 123 52	633.96071	0.002 070 89	733.25915	0.002 845 62
4.4901492	− 0.076 451 13	9.7450770	− 0.078 926 58	95.365382	0.013 740 84	111.11570	0.018 665 75
0.86683800	− 0.191 717 14	2.0046429	− 0.209 520 43	21.003506	0.039 894 34	24.797332	0.053 193 10
0.06301466	0.684 843 84	0.15084819	0.623 612 63	1.6945210	− 0.129 153 42	2.2024956	− 0.157 966 30
0.02432363	0.389 591 68	0.05132907	0.462 626 02	0.49846427	− 0.195 061 04	0.78358637	− 0.232 100 64
				0.05949755	0.625 362 88	0.10873618	0.613 244 20
				0.02368639	0.474 787 40	0.03953124	0.510 020 80

Potassium		Calcium		Rubidium		Strontium	
Exp.	Coeff.	Exp.	Coeff.	Exp.	Coeff.	Exp.	Coeff.
$4s$		$4s$		$5s$		$5s$	
1932.4749	− 0.001 018 22	2129.6339	− 0.001 342 22	7633.6364	0.000 489 53	7955.4511	0.000 645 34
292.02471	− 0.006 879 10	322.87196	− 0.009 038 83	1155.1872	0.003 378 44	1209.9954	0.004 417 75
65.655917	− 0.020 544 85	72.898054	− 0.026 980 91	262.57737	0.010 561 54	276.68668	0.013 727 29
6.5136035	0.065 761 86	7.1428307	0.099 502 37	29.610824	− 0.035 252 12	30.450627	− 0.053 137 49
3.3934779	0.062 847 63	3.3648690	0.080 928 61	16.657120	− 0.028 431 97	15.111309	− 0.035 663 31
0.67828972	− 0.204 772 20	0.96499143	− 0.202 239 12	5.2011014	0.042 669 67	5.8239675	0.067 413 59
0.23717359	− 0.265 258 00	0.39894457	− 0.354 214 33	2.7577627	0.136 119 16	2.8667645	0.182 361 92
0.03972228	0.651 902 91	0.06199958	0.705 640 29	0.48171973	− 0.265 206 89	0.64697193	− 0.250 274 60
0.01716464	0.488 986 20	0.02489404	0.451 176 32	0.17569586	− 0.279 182 94	0.30143269	− 0.377 318 17
				0.03742569	0.613 815 28	0.05188388	0.731 931 14
				0.01626636	0.557 776 58	0.02145642	0.445 804 27

(B) B to Ne

Boron		Carbon		Nitrogen	
Exp.	Coeff.	Exp.	Coeff.	Exp.	Coeff.
$2s$		$2s$		$2s$	
111.57100	− 0.013 349 83	168.58141	− 0.013 482 20	234.34567	− 0.013 706 37
16.708828	− 0.083 049 25	25.318617	− 0.085 275 91	35.371075	− 0.087 089 59
3.5225174	− 0.225 942 93	5.4255585	− 0.234 339 04	7.6916772	− 0.239 166 44
0.27434282	0.627 975 67	0.42924874	0.627 947 87	0.61671684	0.626 808 78
0.09031822	0.462 945 69	0.13817391	0.465 616 33	0.19525028	0.468 703 64
$2p$		$2p$		$2p$	
12.668756	0.012 212 36	19.101229	0.013 619 64	26.846803	0.014 502 17
2.7526026	0.075 256 70	4.2220551	0.084 810 67	6.0006883	0.090 889 50
0.78237754	0.268 305 71	1.2235411	0.286 237 85	1.7568722	0.296 986 58
0.24780086	0.504 885 49	0.38949621	0.501 444 17	0.55944696	0.498 769 84
0.07910665	0.366 736 01	0.12251124	0.348 979 68	0.17366286	0.339 212 32

Oxygen		Fluorine		Neon	
Exp.	Coeff.	Exp.	Coeff.	Exp.	Coeff.
$2s$		$2s$		$2s$	
314.68667	− 0.013 753 22	405.47716	− 0.013 805 19	508.43671	− 0.013 807 48
47.486161	− 0.088 347 23	61.236864	− 0.089 245 06	76.800113	− 0.089 784 24
10.389088	− 0.244 489 83	13.471177	− 0.247 937 86	16.956371	− 0.250 408 80
0.84012567	0.630 868 93	1.0951737	0.632 895 34	1.3812111	0.634 211 22
0.26315314	0.466 049 77	0.34008475	0.465 026 34	0.42583795	0.464 401 42
$2p$		$2p$		$2p$	
34.783409	0.015 717 66	44.136009	0.016 534 82	55.256489	0.016 902 62
7.8228431	0.098 705 32	9.9825971	0.103 846 53	12.553468	0.106 449 34
2.3009849	0.308 675 59	2.9470827	0.316 092 82	3.7146561	0.319 878 15
0.72184533	0.491 476 37	0.91851118	0.487 635 75	1.1531756	0.485 779 09
0.21547961	0.338 684 52	0.26852135	0.336 022 56	0.33248282	0.334 982 19

TABLE II. (*continued*).

(C) Al to Ar

Aluminum		Silicon		Phosphorus	
Exp.	Coeff.	Exp.	Coeff.	Exp.	Coeff.
3s		*3s*		*3s*	
869.14539	0.003 489 72	1019.3882	0.003 926 16	1182.6558	0.004 252 47
131.41377	0.023 077 51	154.03267	0.026 113 52	178.71813	0.028 403 70
29.331438	0.066 236 01	34.403481	0.075 664 80	39.959861	0.083 068 99
2.7348916	− 0.186 881 40	3.2562014	− 0.214 878 53	3.7626176	− 0.249 285 70
1.0890329	− 0.270 690 88	1.3953933	− 0.287 407 06	1.6832762	− 0.288 240 73
0.16806251	0.666 608 38	0.23467257	0.686 551 75	0.31154276	0.691 854 96
0.06112679	0.475 934 21	0.08541769	0.469 942 08	0.11338554	0.477 622 75
3p		*3p*		*3p*	
41.127803	− 0.013 367 45	52.171886	− 0.014 783 59	63.656661	− 0.015 722 46
9.1225875	− 0.066 023 23	11.684958	− 0.075 567 57	14.381855	− 0.081 979 90
2.4017227	− 0.122 471 28	3.1630276	− 0.145 757 56	3.9821550	− 0.161 699 38
0.22215689	0.360 851 75	0.31961955	0.398 061 00	0.43364640	0.411 825 46
0.08312327	0.532 001 73	0.12188821	0.521 482 33	0.16910055	0.511 817 22
0.03278319	0.231 727 33	0.04832592	0.201 606 41	0.06736732	0.195 870 20

Sulfur		Chlorine		Argon	
Exp.	Coeff.	Exp.	Coeff.	Exp.	Coeff.
3s		*3s*		*3s*	
1358.5662	0.004 527 64	1542.3787	0.004 765 90	1732.7206	0.004 988 66
205.28669	0.030 359 31	233.13204	0.032 037 56	261.83186	0.033 616 23
45.947830	0.089 508 18	52.247074	0.094 965 42	58.751949	0.099 822 12
4.2713728	− 0.291 467 37	4.8942113	− 0.316 640 11	5.7019860	− 0.313 480 69
1.9346495	− 0.280 241 16	2.2817665	− 0.275 631 67	2.8272408	− 0.286 784 74
0.40302707	0.694 747 49	0.49147978	0.708 946 76	0.57143478	0.731 710 12
0.14580296	0.490 363 16	0.17766657	0.482 421 92	0.20740807	0.455 911 09
3p		*3p*		*3p*	
77.325536	− 0.016 004 61	92.088394	− 0.016 221 37	107.45459	− 0.016 239 44
17.559142	− 0.085 601 39	20.986022	− 0.088 632 08	24.590709	− 0.090 018 90
4.9407281	− 0.174 097 13	5.9753203	− 0.184 713 28	7.0801889	− 0.190 833 02
0.56098162	0.419 760 95	0.69826911	0.429 956 50	0.85360221	0.434 311 54
0.21373625	0.505 873 52	0.26378791	0.501 543 59	0.32321813	0.498 882 04
0.08211480	0.201 743 21	0.09973113	0.198 681 08	0.12131460	0.198 540 20

(D) Ga to Kr

Gallium		Germanium		Arsenic	
Exp.	Coeff.	Exp.	Coeff.	Exp.	Coeff.
4s		*4s*		*4s*	
5367.4306	− 0.001 476 56	5719.4050	− 0.001 651 34	6111.3583	− 0.001 789 00
811.36777	− 0.010 164 97	865.76338	− 0.011 356 25	925.47074	− 0.012 312 05
183.72308	− 0.031 635 83	196.33225	− 0.035 401 66	209.94118	− 0.038 562 59
18.642715	0.135 953 64	20.024532	0.151 082 84	21.126459	0.172 248 84
6.8523494	0.110 786 42	8.2760821	0.088 086 11	7.6613551	0.121 628 57
3.7921403	− 0.214 869 40	3.6906203	− 0.217 222 67	4.2391524	− 0.261 215 25
1.3684228	− 0.369 813 54	1.5100934	− 0.399 557 29	1.6977212	− 0.440 475 85
0.18290436	0.682 578 13	0.23155743	0.708 013 54	0.28128340	0.724 897 76
0.06613904	0.463 086 80	0.08521711	0.458 506 83	0.10507290	0.458 208 78
4p		*4p*		*4p*	
427.90531	0.002 821 57	457.76219	0.003 460 60	494.19603	0.003 894 19
99.751825	0.017 621 52	106.97527	0.021 597 69	115.30478	0.024 538 65
30.462408	0.042 636 92	32.809328	0.052 206 36	35.358226	0.059 759 32
4.1704945	− 0.101 177 62	4.5650328	− 0.123 255 37	4.9811154	− 0.139 798 77
1.6675248	− 0.107 937 25	1.8685617	− 0.132 453 69	2.0933920	− 0.150 653 77
0.27998301	0.262 815 82	0.35217114	0.301 195 39	0.42612145	0.327 993 96
0.10606878	0.541 523 66	0.14102761	0.546 545 93	0.17653942	0.546 605 76
0.03900144	0.337 412 02	0.05384002	0.290 453 58	0.06903644	0.262 790 45

TABLE II. (*continued*).

Selenium		Bromine		Krypton	
Exp.	Coeff.	Exp.	Coeff.	Exp.	Coeff.
4s		**4s**		**4s**	
6463.6063	− 0.001 935 55	6861.1369	− 0.002 052 45	7274.6460	− 0.002 156 41
978.65832	− 0.013 327 16	1039.1071	− 0.014 138 98	1101.3186	− 0.014 874 50
222.15825	− 0.041 639 12	235.99404	− 0.044 271 21	250.14039	− 0.046 668 41
22.995560	0.177 640 13	24.515665	0.189 025 67	26.115038	0.198 817 70
8.8758569	0.143 427 10	9.6230243	0.148 426 81	10.547979	0.145 764 37
5.0477639	− 0.242 432 88	5.4592327	− 0.245 314 40	5.7826331	− 0.242 918 57
1.9942748	− 0.504 864 01	2.2239019	− 0.538 741 84	2.4592535	− 0.565 353 68
0.32451172	0.763 669 01	0.37657260	0.780 126 75	0.43065898	0.793 370 94
0.12213454	0.427 445 46	0.14269568	0.422 877 10	0.16421502	0.419 943 05
4p		**4p**		**4p**	
527.38399	0.004 300 34	558.27094	0.004 716 77	594.54256	0.004 976 84
123.19240	0.027 138 57	130.71326	0.029 676 19	139.37944	0.031 371 22
37.884859	0.066 101 98	40.382765	0.071 889 86	43.167513	0.076 213 95
5.4549154	− 0.150 265 65	5.9729582	− 0.158 180 68	6.4507830	− 0.167 167 34
2.3912365	− 0.164 549 72	2.7088715	− 0.178 893 92	2.9957592	− 0.187 491 83
0.49253341	0.366 835 56	0.56468401	0.392 997 44	0.64875622	0.406 292 35
0.20000361	0.536 913 51	0.22905019	0.529 907 53	0.26490030	0.527 537 44
0.07705436	0.240 895 86	0.08826465	0.224 389 79	0.10238135	0.215 992 47

(E) In to Xe

Indium		Tin		Antimony	
Exp.	Coeff.	Exp.	Coeff.	Exp.	Coeff.
5s		**5s**		**5s**	
13627.123	0.000 865 69	14318.859	0.000 949 30	14986.049	0.001 020 19
2066.3491	0.006 005 20	2164.7627	0.006 622 79	2268.0036	0.007 116 40
471.46731	0.019 198 77	492.42833	0.021 297 64	515.91639	0.023 025 35
51.977294	− 0.079 009 47	53.682666	− 0.092 869 52	54.556398	− 0.109 638 94
28.177340	− 0.043 311 11	26.194980	− 0.050 110 56	23.737928	− 0.049 368 00
11.316458	0.054 271 97	10.635987	0.142 280 61	9.7889291	0.283 611 64
6.7990435	0.274 715 13	6.3514585	0.247 923 78	4.9383988	0.194 240 26
1.6387888	− 0.314 439 55	2.0207246	− 0.267 762 34	2.3916960	− 0.313 735 99
0.83564379	− 0.363 800 97	1.0112193	− 0.492 430 35	1.1202396	− 0.559 248 32
0.14681625	0.703 805 48	0.17433614	0.752 144 12	0.20747927	0.769 962 26
0.05518918	0.480 944 94	0.06723016	0.449 730 89	0.08145485	0.454 275 41
5p		**5p**		**5p**	
1180.4919	− 0.001 596 41	1247.5155	− 0.001 874 25	1304.1881	− 0.002 105 75
278.99391	− 0.010 324 74	294.54323	− 0.012 215 33	308.62796	− 0.013 715 41
88.221611	− 0.025 920 87	93.013946	− 0.031 076 21	97.641074	− 0.035 090 65
14.606078	0.055 322 88	14.870982	0.075 397 19	15.143351	0.097 589 12
8.3707565	0.058 465 85	8.3471621	0.062 639 21	7.7883798	0.066 463 35
2.2319513	− 0.143 657 43	2.4478151	− 0.168 060 29	2.8819722	− 0.166 185 11
1.0127837	− 0.149 169 47	1.1301888	− 0.183 688 68	1.3422826	− 0.231 365 26
0.20969314	0.274 017 79	0.25407901	0.314 969 77	0.28309803	0.377 635 73
0.08624411	0.548 857 33	0.11000992	0.553 907 75	0.12688673	0.536 828 03
0.03360312	0.315 733 62	0.04452413	0.270 622 62	0.05365244	0.222 138 61

Tellurium		Iodine		Xenon	
Exp.	Coeff.	Exp.	Coeff.	Exp.	Coeff.
5s		**5s**		**5s**	
15458.761	0.001 103 30	15994.065	0.001 174 27	16687.518	0.001 228 13
2343.3283	0.007 672 16	2426.8433	0.008 154 29	2528.8588	0.008 550 58
534.53546	0.024 699 91	554.27300	0.026 199 58	576.90821	0.027 572 71
57.142954	− 0.117 303 26	59.962846	− 0.122 632 60	62.142131	− 0.131 038 26
23.440839	− 0.067 421 63	24.081946	− 0.087 954 46	24.161520	− 0.100 889 03
11.191278	0.271 090 96	12.616574	0.270 665 16	13.440541	0.291 880 29
5.5785498	0.279 759 31	6.0282860	0.347 974 78	6.2971297	0.401 007 75
2.9520152	− 0.279 297 80	3.2896136	− 0.299 427 89	3.7813986	− 0.310 613 87
1.3006989	− 0.667 691 98	1.4196077	− 0.721 497 60	1.5715446	0.785 654 54
0.23364289	0.817 151 82	0.26820688	0.832 183 47	0.29920022	0.854 840 28
0.09239681	0.418 084 42	0.10699673	0.421 840 32	0.12027958	0.410 595 94

TABLE II. (*continued*).

Tellurium		Iodine		Xenon	
Exp.	Coeff.	Exp.	Coeff.	Exp.	Coeff.
5p		*5p*		*5p*	
1368.1531	− 0.002 297 92	1429.3411	− 0.002 480 08	1495.0478	− 0.002 599 50
322.98386	− 0.015 064 64	337.68320	− 0.016 303 44	353.14067	− 0.017 152 18
102.14783	− 0.038 705 61	106.76853	− 0.042 118 16	111.65084	− 0.044 589 26
15.763006	0.112 271 20	16.529856	0.122 926 33	17.179532	0.134 549 65
7.6127910	0.079 693 11	7.9342416	0.088 930 23	7.9202922	0.100 431 96
3.4346177	− 0.158 908 90	3.7719165	− 0.164 929 09	4.1867763	− 0.175 154 39
1.5816834	− 0.278 055 09	1.7516178	− 0.307 211 52	1.9257668	− 0.331 921 57
0.31078766	0.446 416 97	0.35460546	0.465 222 39	0.39798013	0.487 262 17
0.13334331	0.516 781 42	0.15225035	0.510 841 43	0.17064828	0.506 711 97
0.05589872	0.178 311 81	0.06367669	0.170 669 53	0.07146247	0.156 709 22

tions. The results of the MP basis sets for which only the innermost primitives were optimized (dashed line) show slower convergence. The values of all properties (valence energy, valence orbital energies, and orbital shapes) seem to reach a stable point at $n = 5$ and the basis set $(5_{32}/5)$ shows an excellent agreement with the HF values.

In order to assess the importance of the number of inner primitives on the molecular results, a series of AE and MP calculations were carried out on $N_2(^1\Sigma_g^+)$, for which the valence part of both AE and MP basis sets are equivalent. A $(W3_{12}/5)$ basis set was used in the AE calculation and the $(n_{n-2,2}/5)$ basis sets in the MP calculations; single s, p splitting, double p splitting, double p splitting plus single polarization, and double p splitting plus double polarization were tested in all the cases; the results are shown in Fig. 3. It is evident that the MP values of the equilibrium distance R_e, vibrational frequency $\bar{\nu}_e$, and atomization energy D_e converge to the AE ones obtained with an equivalent valence part and that the agreement is already very good for the (5/5)-type basis sets. This, together with the atomic results, suggests the use of the $(5_{32}/5)$ basis sets for N and the first row elements. In Tables II(A) and II(B) we present the optimized (5/5) basis sets for the first row elements; the corresponding atomic properties are shown in Table III(A). [In the Table, E(proj) stands for the expectation value of the core projector operator, Eq. (3), with the MP atomic wave function, and measures the degree of core–valence orthogonality achieved.]

In Figs. 4 and 5 we show atomic MP results on $P(^4S)$. They converge to the MP$(WW3_{12}/W3_3)$ results, for which the $1s$, $2s$, and $2p$ WT atomic orbitals[14] were used as inner contracted functions and the three outermost primitives s and p were optimized in AE calculations. The results $(5_{212}/n)$, $(6_{222}/n)$, and $(7_{322}/n)$, show that the presence of a third primitive s whose main role is to augment the $3s$–$1s$ orthogonality is more important than the presence of a second primitive s whose purpose is to increase the $3s$–$2s$ orthogonality.

Although the $(5_{212}/n)$ basis sets give results which are close enough to the HF values to be acceptable, the $(7_{322}/n)$-type basis sets provide a higher core–valence orthogonality and, at the same time, do not increase the number of basis set

functions in molecular calculations. So, we optimized the $(7_{322}/6_{33})$ basis sets fo the elements Na to Ar and we present them in Tables II(A) and II(C). The corresponding energies and radial expectation values appear in Table III(B).

Similar basis sets, also capable of leading to a high degree of core–valence orthogonality, were optimized for the main group elements from K to Kr and from Rb to Xe. All of them, as well as their atomic MP results are collected in Tables II(A), II(D), II(E), III(C), and III(D).

IV. MOLECULAR CALCULATIONS

In this section we present the results of the MP SCF molecular calculations carried out using the MP parameters and basis sets in Tables I and II in order to test the performance of the method. The equilibrium distance R_e, vibrational frequency $\bar{\nu}_e$, and atomization energy D_e have been calculated for the ground states of N_2, P_2, As_2, and Sb_2, as well as for CaO. The different basis sets used in the calculations on N_2, P_2, As_2, and Sb_2 appear in Table IV. Since we regard the final goal of a valence method to be the reproduction of the AE results if the same kind of wave function and valence basis set is used, rather than the reproduction of the AE results using a poorer valence basis set, we grouped the molecular basis sets (Table IV) in such a way that for each AE basis set there is an MP one having the same structure in the valence space. So, we have basis sets A, corresponding to a single s, p splitting of the outermost contracted functions, basis sets B, obtained from A by a double p splitting, basis sets C, which result from the addition of a single d-polarization function to B, and basis sets D, resulting from the addition of two d-polarization functions to B. In the AE basis sets for N, P, and As, we used the well-tempered core orbitals[14] as inner contracted functions and we optimized the outermost contracted functions in atomic calculations; the AE basis set for Sb was taken from Ref. 13. All the polarization functions were taken from Ref. 13.

The AE and MP molecular results are presented in Table V. They are also plotted in Fig. 6, where it is clear that the valence basis set dependence shown by the AE results (solid lines) is reproduced in the MP calculations (discontinuous lines). For As_2 and Sb_2 the MP results reproduce the effects

TABLE III. Valence energy, projection energy, valence orbital energies, and valence orbital radial expectation values for the main group elements. All numbers in atomic units.

(A) Li to Ne

		$E(\text{val})$	$E(\text{proj})$	$\epsilon(2s)$	$\epsilon(2p)$	2s			2p		
						$\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$
	HF			− 0.196 323		0.345	3.874	17.738			
Li	MP(5)	− 0.195 531	0.000 002	− 0.195 531		0.343	3.889	17.877			
	HF			− 0.309 270		0.523	2.649	8.426			
Be	MP(5)	− 0.958 673	0.000 022	− 0.308 260		0.518	2.657	8.464			
	HF			− 0.494 706	− 0.309 856	0.713	1.977	4.709	0.605	2.205	6.146
B	MP(5/5)	− 2.536 860	0.000 032	− 0.492 172	− 0.310 634	0.707	1.983	4.731	0.606	2.197	6.076
	HF			− 0.705 627	− 0.433 341	0.897	1.589	3.052	0.784	1.714	3.747
C	MP(5/5)	− 5.318 287	0.000 046	− 0.701 437	− 0.433 776	0.889	1.594	3.065	0.784	1.709	3.707
	HF			− 0.945 324	− 0.567 589	1.078	1.332	2.149	0.958	1.410	2.548
N	MP(5/5)	− 9.651 911	0.000 063	− 0.939 137	− 0.567 584	1.069	1.336	2.157	0.958	1.405	2.520
	HF			− 1.244 315	− 0.631 906	1.265	1.142	1.581	1.111	1.232	1.975
O	MP(5/5)	− 15.680 396	0.000 081	− 1.235 359	− 0.630 843	1.255	1.145	1.587	1.112	1.228	1.949
	HF			− 1.572 535	− 0.730 017	1.450	1.001	1.217	1.272	1.085	1.544
F	MP(5/5)	− 23.899 450	0.000 102	− 1.560 434	− 0.727 745	1.438	1.004	1.221	1.272	1.081	1.521
	HF			− 1.930 391	− 0.850 410	1.633	0.892	0.967	1.435	0.965	1.228
Ne	MP(5/5)	− 34.655 314	0.000 125	− 1.914 655	− 0.846 682	1.619	0.894	0.970	1.436	0.961	1.209

(B) Na to Ar

		$E(\text{val})$	$E(\text{proj})$	$\epsilon(3s)$	$\epsilon(3p)$	3s			3p		
						$\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$
	HF			− 0.182 103		0.310	4.209	20.705			
Na	MP(7)	− 0.181 387	0.000 004	− 0.181 387		0.299	4.224	20.837			
	HF			− 0.253 053		0.399	3.253	12.419			
Mg	MP(7)	− 0.782 588	0.000 015	− 0.252 285		0.397	3.260	12.459			
	HF			− 0.393 420	− 0.209 951	0.507	2.599	7.891	0.379	3.434	14.006
Al	MP(7/6)	− 1.874 278	0.000 025	− 0.392 567	− 0.209 408	0.504	2.604	7.911	0.378	3.442	14.063
	HF			− 0.539 841	− 0.297 115	0.603	2.207	5.676	0.478	2.752	8.981
Si	MP(7/6)	− 3.670 451	0.000 039	− 0.538 777	− 0.296 571	0.600	2.211	5.689	0.476	2.757	9.009
	HF			− 0.696 415	− 0.391 708	0.695	1.933	4.347	0.570	2.323	6.390
P	MP(7/6)	− 6.345 365	0.000 088	− 0.695 044	− 0.391 175	0.690	1.936	4.356	0.568	2.326	6.404
	HF			− 0.879 527	− 0.437 369	0.786	1.721	3.443	0.651	2.061	5.065
S	MP(7/6)	− 9.936 552	0.000 060	− 0.877 540	− 0.436 806	0.781	1.724	3.450	0.649	2.063	5.074
	HF			− 1.072 910	− 0.506 400	0.875	1.556	2.813	0.733	1.842	4.059
Cl	MP(7/6)	− 14.715 819	0.000 098	− 1.070 322	− 0.505 833	0.869	1.558	2.819	0.732	1.844	4.064
	HF			− 1.277 353	− 0.591 017	0.962	1.422	2.350	0.814	1.663	3.311
Ar	MP(7/6)	− 20.848 220	0.000 134	− 1.274 434	− 0.590 578	0.956	1.424	2.355	0.812	1.664	3.313

(C) K to Kr

		$E(\text{val})$	$E(\text{proj})$	$\epsilon(4s)$	$\epsilon(4p)$	4s			4p		
						$\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$
	HF			− 0.147 475		0.237	5.244	31.545			
K	MP(9)	− 0.146 790	0.000 004	− 0.146 790		0.235	5.264	31.777			
	HF			− 0.195 530		0.300	4.218	20.453			
Ca	MP(9)	− 0.603 857	0.000 011	− 0.194 996		0.298	4.228	20.534			
	HF			− 0.424 592	− 0.208 500	0.516	2.489	7.207	0.372	3.424	13.901
Ga	MP(9/8)	− 1.960 596	0.000 037	− 0.423 006	− 0.208 101	0.513	2.493	7.227	0.372	3.426	13.896
	HF			− 0.553 364	− 0.287 354	0.579	2.226	5.731	0.446	2.867	9.657
Ge	MP(9/8)	− 3.628 237	0.000 044	− 0.551 973	− 0.287 198	0.576	2.229	5.740	0.445	2.866	9.645
	HF			− 0.685 897	− 0.369 483	0.638	2.030	4.748	0.510	2.512	7.372
As	MP(9/8)	− 6.006 316	0.000 069	− 0.684 092	− 0.369 303	0.634	2.033	4.757	0.509	2.513	7.368
	HF			− 0.837 382	− 0.402 855	0.695	1.869	4.015	0.563	2.300	6.196
Se	MP(9/8)	− 9.081 871	0.000 070	− 0.835 260	− 0.402 703	0.692	1.872	4.024	0.562	2.300	6.194
	HF			− 0.992 681	− 0.457 086	0.751	1.739	3.468	0.617	2.112	5.224
Br	MP(9/8)	− 13.060 113	0.000 113	− 0.990 258	− 0.456 991	0.747	1.741	3.475	0.617	2.112	5.221
	HF			− 1.152 935	− 0.524 187	0.804	1.629	3.040	0.669	1.952	4.455
Kr	MP(9/8)	− 18.040 353	0.000 102	− 1.150 346	− 0.524 159	0.800	1.632	3.046	0.668	1.952	4.453

TABLE III. (*continued*).

(D) Rb to Xe

		E(val)	E(proj)	ε(5s)	ε(5p)	5s ⟨1/r⟩	5s ⟨r⟩	5s ⟨r²⟩	5p ⟨1/r⟩	5p ⟨r⟩	5p ⟨r²⟩
	HF			− 0.137 867		0.218	5.632	36.179			
Rb	MP(11)	− 0.137 436	0.000 005	− 0.137 436		0.217	5.643	36.309			
	HF			− 0.178 456		0.269	4.633	24.497			
Sr	MP(11)	− 0.550 414	0.000 009	− 0.177 901		0.267	4.643	24.598			
	HF			− 0.372 663	− 0.197 283	0.445	2.844	9.305	0.332	3.778	16.647
In	MP(11/10)	− 1.743 427	0.000 041	− 0.372 066	− 0.197 198	0.443	2.845	9.303	0.332	3.774	16.605
	HF			− 0.476 435	− 0.265 040	0.490	2.586	7.646	0.387	3.248	12.194
Sn	MP(11/10)	− 3.177 429	0.000 041	− 0.475 738	− 0.265 013	0.489	2.587	7.648	0.387	3.246	12.172
	HF			− 0.581 773	− 0.334 711	0.532	2.390	6.507	0.434	2.901	9.668
Sb	MP(11/10)	− 5.190 580	0.000 053	− 0.580 841	− 0.334 556	0.530	2.391	6.509	0.434	2.900	9.660
	HF			− 0.700 561	− 0.359 832	0.573	2.228	5.638	0.472	2.691	8.339
Te	MP(11/10)	− 7.753 557	0.000 063	− 0.699 592	− 0.359 878	0.571	2.229	5.641	0.472	2.690	8.329
	HF			− 0.821 116	− 0.403 180	0.611	2.094	4.972	0.510	2.502	7.201
I	MP(11/10)	− 11.027 799	0.000 122	− 0.820 007	− 0.403 354	0.609	2.095	4.974	0.511	2.500	7.190
	HF			− 0.944 414	− 0.457 290	0.648	1.981	4.440	0.547	2.338	6.277
Xe	MP(11/10)	− 15.081 571	0.000 070	− 0.943 455	− 0.457 627	0.646	1.982	4.441	0.547	2.336	6.267

of the polarization functions (basis sets C and D; dotted lines in Fig. 6) not as closely as they reproduce the effects of splitting, though the differences are still acceptable. This small deficiency has been found to be due to insufficient orthogonality between the valence molecular orbitals and the d core orbitals, as a consequence of the presence of d polarization functions. If the ability of the valence molecular orbitals to be orthogonal to the $3d$ core orbitals (on As) or to the $4d$ core orbitals (on Sb) is increased by adding inner contracted functions representing the $3d$ or $4d$ orbitals[13] (see Table IV,
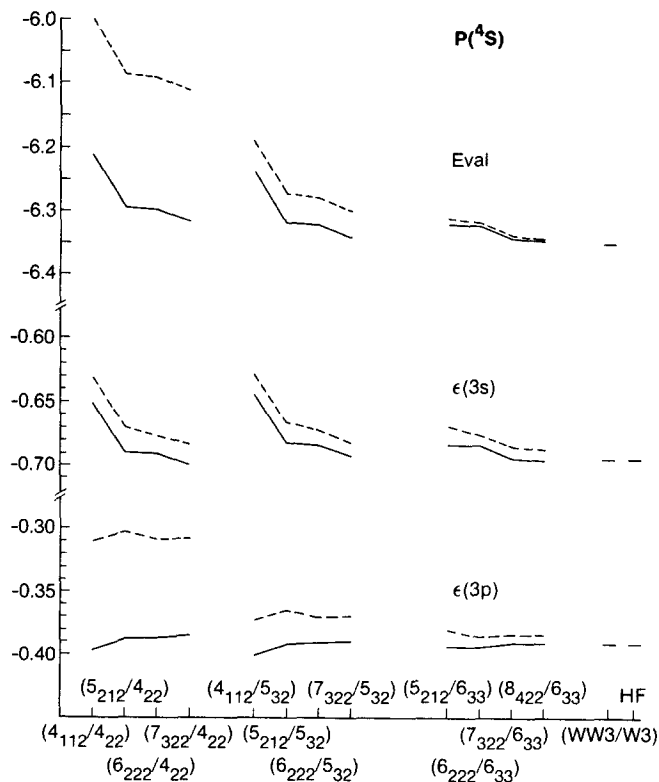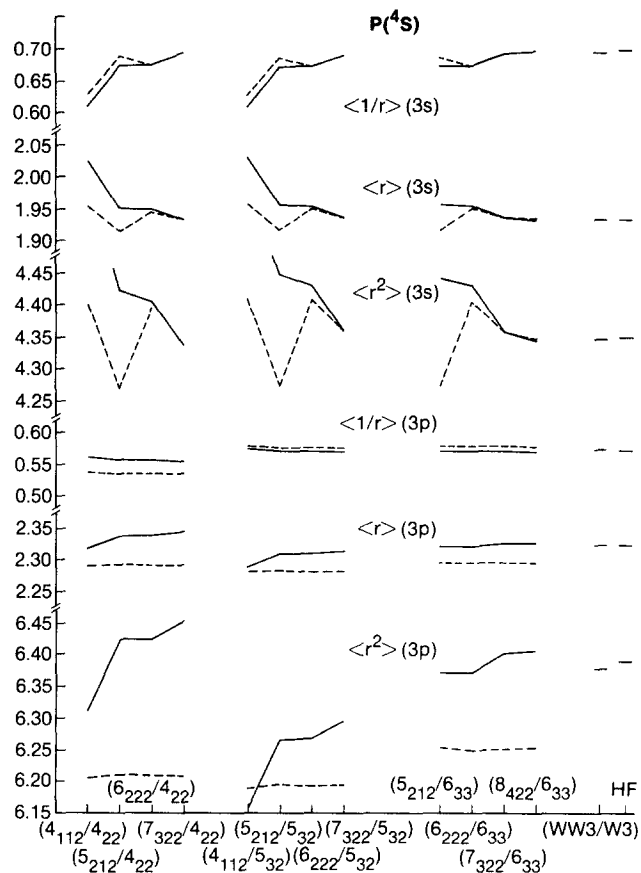

FIG. 4. Valence and orbital energies for P(^4S), in a.u. Solid line: completely optimized valence basis set; dashed line: only the innermost primitives were optimized.

FIG. 5. Radial expectation values for the valence orbitals of P(^4S) in a.u Solid line: completely optimized valence basis set; dashed line: only the innermost primitives were optimized.

TABLE IV. AE and MP basis sets used in the molecular calculations on N_2, P_2, As_2, and Sb_2.

Atom		Basis sets[a]			
		A	B	C	D
N	AE	$(W21/41)$	$(W21/311)$	$(W21/311/1*)$	$(W21/311/1*1*)$
	MP	$(41/41)$	$(41/311)$	$(41/311/1*)$	$(41/311/1*1*)$
P	AE	$(WW21/W21)$	$(WW21/W111)$	$(WW21/W111/1*)$	$(WW21/W111/1*1*)$
	MP	$(61/51)$	$(61/411)$	$(61/411/1*)$	$(61/411/1*1*)$
As	AE	$(WWW21/WW21/W)$	$(WWW21/WW111/W)$	$(WWW21/WW111/W1*)$	$(WWW21/WW111/W1*1*)$
	MP	$(711/521)$	$(711/5111)$	$(711/5111/1*)$ C_2: $(711/5111/31*)$	$(711/5111/1*1*)$ D_2:$(711/5111/31*1*)$
Sb	AE	$(433321/43321/43)$	$(433321/433111/43)$	$(433321/433111/431*)$	$(433321/433111/431*1*)$
	MP	$(911/721)$	$(911/7111)$	$(911/7111/1*)$ C_2:$(911/7111/31*)$	$(911/7111/1*1*)$ D_2:$(911/7111/31*1*)$

[a] W stands for the corresponding well-tempered atomic core atomic orbitals (Ref. 13) taken as contracted functions.

bases C_2 and D_2), the AE trends are again reproduced very closely by the MP results (see Table V MP C_2 and MP D_2, and dashed lines in Fig. 6). (Note that the molecular MP calculations are always ten-electron calculations.) It should be noticed, though, that the discrepancies between the results of AE and MP calculations that do not include such inner functions are of the order of 0.01 Å for R_e, 20 cm^{-1} for $\bar{v}_e$, and 0.2 eV for D_e in N_2, P_2, and As_2, and of the order of 0.03 Å for R_e, 20 cm^{-1} for $\bar{v}_e$, and 0.5 eV for D_e in Sb_2. This insufficient core–valence orthogonality, originating from the addition of polarization functions to blocks having core orbitals but no inner components in the basis set, should be encountered not only when using the present MP formulation but in *any* valence method which assumes strong core–valence orthogonality properties in its formulation. What is characteristic to the present formulation is that the high quality of the core operators used and, hence, the close re-

production of AE basis set dependencies, were able to point out such a subtle effect.

In Table VI we present the results for $CaO(^1\Sigma^+)$. Valence calculations on this molecule often result in very large errors for R_e[10] or even collapse[4]; these results have been interpreted as due to participation of the Ca $3p$ orbitals in the bonding.

We have performed AE SCF calculations on $CaO(^1\Sigma^+)$ with two kind of basis sets (Table IV) which differ in the valence space. In the first one, only s and p functions are used in Ca[13] and only s splitting is considered, $(43321/43)$, which means that the participation of the Ca $3p$ orbitals in the bonding is very restricted. As a result, a very large value for R_e is obtained, 2.326 Å. The corresponding MP calculation with only s functions in Ca, (81), gives a value of 2.663 Å, which is corrected to 2.337 Å if a 2-primitive contracted p function which maximizes the overlap with

TABLE V. AE and MP calculated values of R_e, $\bar{v}_e$, and D_e for N_2, P_2, As_2, and Sb_2.

|		N_2			P_2			As_2			Sb_2		
		R_e/Å	$\bar{v}_e$/cm^{-1}	D_e/eV	R_e/Å	$\bar{v}_e$/cm^{-1}	D_e/eV	R_e/Å	$\bar{v}_e$/cm^{-1}	D_e/eV	R_e/Å	$\bar{v}_e$/cm^{-1}	D_e/eV
AE	A	1.098	2609	2.52	1.949	807	−0.69	2.134	464	−0.99	2.530	301	−1.23
MP	A	1.102	2636	2.53	1.991	794	−1.30	2.146	454	−1.08	2.558	287	−1.67
AE	B	1.086	2558	2.73	1.941	792	−0.66	2.121	456	−0.95	2.517	298	−1.19
MP	B	1.091	2566	2.70	1.945	786	−0.94	2.135	449	−1.05	2.547	285	−1.64
AE	C	1.072	2728	4.89	1.876	901	1.25	2.070	509	0.40	2.464	331	−0.13
MP	C	1.079	2746	4.86	1.877	906	1.16	2.075	516	0.71	2.474	332	0.08
MP	C_2							2.067	511	0.58	2.492	314	−0.65
AE	D	1.066	2725	5.04	1.862	905	1.47	2.066	508	0.47	2.462	329	−0.12
MP	D	1.068	2729	5.09	1.858	914	1.36	2.081	497	0.19	2.494	320	−0.65
MP	D_2							2.065	509	0.55	2.496	313	−0.71
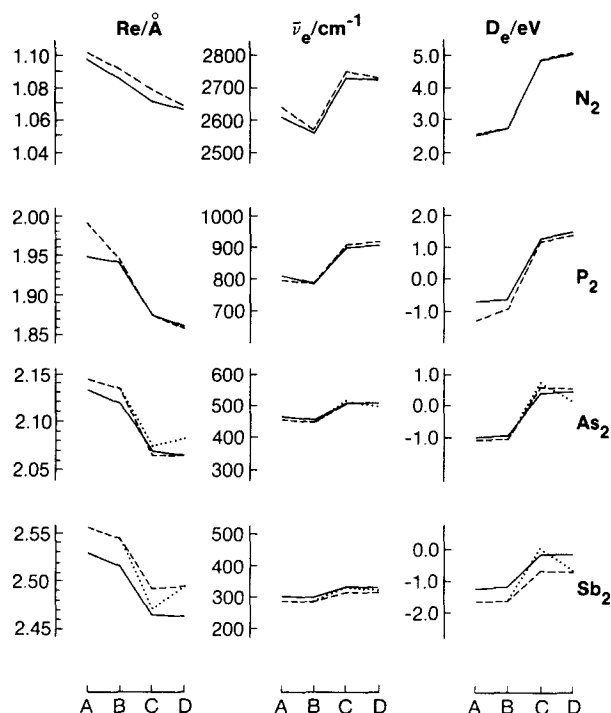
FIG. 6. AE and MP equilibrium distances (R_e), vibrational frequencies $(\bar{\nu}_e)$, and atomization energies (D_e) for N_2, P_2, As_2, and Sb_2. The solid line stands for the AE results, the dotted and dashed lines stand for the MP results without and with internal d functions, respectively. See the text and Table IV for the description of basis sets A, B, C, and D.

the outermost p contracted in the Ca AE basis set is used, (81/2). This result reveals, first, that the MP method is capable of reproducing the results of AE calculations in which the participation of the $3p$ orbitals in the bonding is considerably restricted, and, second, that the presence in the molecular valence basis set of inner functions able to provide a high degree of orthogonality between the molecular valence orbitals and the core orbitals (in this case Ca $3p$) is important in that respect.

If p splitting is allowed in Ca and polarization functions are added, as well as $3d$ functions which have been proven important in Ca compounds,[16] the AE results change very

much, particularly R_e is reduced by 0.50 Å to the value 1.827 Å. The same kind of manipulation in the MP basis set produces a very close effect, lowering by 0.45 Å the value of R_e, $R_e = 1.788$ Å, being the discrepancy with the AE result of 0.04 Å. This error, larger than those in other molecules, could probably be associated to a *certain* degree of Ca $3p$ participation in the bonding, which could also be responsible for the rather poor value of D_e.

V. CONCLUSIONS

In this paper we presented the nonrelativistic *ab initio* model potential method. The *ab initio* attribute stem from the following features: (i) the Coulomb and exchange core operators J_c and K_c are modeled through accurate local and nonlocal forms, respectively, (ii) since the model potential operators closely represent physical core–valence interactions, their parameters are *never* used to accomodate effects of reduction on the valence basis set nor deficiencies in the molecular results, (iii) the design and optimization of the model potential basis set is a replica of the design and optimization of all-electron atomic basis sets.

The results of the test molecular calculations show the good performance of the method. Particularly important is the conclusion that the effects of changes in the valence basis set observed in the model potential results closely resemble those shown by corresponding all-electron calculations. This aspect reveals not only that the representation of the dormant core electrons accomplished *near AE* quality, but also that all the experience already gathered on the design of molecular basis sets can be used for model potential molecular calculations. In this respect, our results also show that the lack of orthogonality between the core orbitals and the molecular valence orbitals may be detrimental in some cases, and, then, some inner basis set functions able to increase orthogonality must be provided to the molecular basis set.

In this paper we present model potential parameters and optimized valence basis sets suitable for model potential molecular calculations including the main group elements from Li to Xe. The model potential parameters and basis sets for transition metal atoms will be presented in a forthcoming paper.

TABLE VI. AE and MP results for $CaO(^1\Sigma^+)$.

Basis set[a]		R_e/Å	$\bar{\nu}_e$/cm^{-1}	D_e/eV
Ca	O			
AE (43321/43)	(521/311)	2.326	330	− 2.46
MP (81)	(41/311)	2.663	281	− 2.74
MP (81/2)	(41/311)	2.337	365	− 2.47
AE (43321/4211*/311)	(521/3111/1*)	1.827	815	0.48
MP (81/211*/311)	(41/3111/1*)	1.788	750	− 0.43

[a] The AE basis sets were taken from Ref. 12. The Ca $3d$ functions correspond to Ref. 14.

ACKNOWLEDGMENTS

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