

Pseudopotential Calculations for Li₂, Na₂ and NaLi

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Abstract

A valence-electron only model potential (VALMOP) pseudopotential method has been developed utilising the GAUSSIAN 76 integral packages. VALMOP and the reference *ab initio* potential energy curves have been calculated for the ground electronic state of Li₂, Na₂ and NaLi using a number of different basis sets. Comparisons indicate that VALMOP accurately reproduces internuclear bondlengths, valence orbital eigenvalues and, moreover, the shape of the all-electron potential energy curves over a large range of bondlength R .

1. Introduction

Over the last two decades research into valence-only pseudopotential methods has continued unabated (Weeks *et al.* 1969; Krauss and Stevens 1984; Durand and Malrieu 1987). The driving motive behind this research is the need to extend the applicability of molecular orbital (MO) self-consistent field (SCF) Hartree-Fock (HF) calculations to large and electron-dense molecules at a reasonable economic cost. This need has become even more pressing due to recent experimental and theoretical interests in cluster formation and stability (Koutecky and Fantucci 1986).

Pseudopotential methods aim to replace the all-electron Hamiltonian by a suitably modified valence-only Hamiltonian in which the core-valence orthogonality constraint and core-valence interactions are effectively reproduced (Weeks *et al.* 1969; Krauss and Stevens 1984; Durand and Malrieu 1987). Due to the failure of the two-electron operator in the many-valence-electron system to commute with the core projection operator (Huzinaga and Cantu 1971), there have arisen two distinctive approaches to this problem: the first involves the use of angular momentum projection operators and therefore the use of nodeless valence orbitals (e.g. Igel-Mann *et al.* 1987); the second involves the explicit use of the core-valence orthogonality constraint and, therefore, the use of valence orbitals that have (within the limits of an atomic 'frozen-core' approximation) the correct nodal structure within the core region (e.g. Huzinaga *et al.* 1987). Both approaches have their advantages and disadvantages. For example, a distinct advantage of the second approach is that the nodal structure of the valence orbitals is important for computing observables which involve a $1/r^3$ operator (diamagnetic susceptibility), as well as accurately simulating the indirect relativistic corrections. On the other hand, the explicit inclusion of a strong core-valence orthogonality restraint requires a much larger basis set than does the use of nodeless valence orbitals.

Tables 1 and 2 list the VALMOP lithium and sodium parameters respectively, derived from atomic and molecular calculations. The 'core' eigenvalues and eigenfunctions used in equation (4) are obtained from standard atomic unrestricted open-shell calculations. The α values used in equation (6) are obtained from diatomic molecular calculations in which the VALMOP valence eigenvalues are fitted to the corresponding all-electron eigenvalues at the all-electron predicted bondlength. Since in the all-electron formulation the valence eigenvalues can be expressed in terms of a non-local exchange core orbital operator spanned by the valence basis functions, the α must be considered quasi-local in this diatomic formulation.

Table 2. VALMOP sodium pseudopotential and quasi-local potential parameters (all energies and bondlengths in a.u.)

Basis set	$E(\text{core})$	E_{val}	α	R_e^A
STO-6G	1s -40.62768	-0.17075	s 16.250	5.561
	2s -2.75005		p 0.5421	
	2p -1.39203			
6-21G	1s -40.49196	-0.16350	s 16.180	6.047
	2s -2.80731		p 0.4032	
	2p -1.52569			

^A R_e is the bondlength at the all-electron energy minimum.

As anticipated the data show a slight basis set dependence. For example, the lithium core eigenenergies are within $0.08 E_h$ with the STO-6G basis set exhibiting an order of magnitude deviation from the three more flexible basis sets. (Note that throughout this paper the symbol for energy in hartree units is E_h .) However, for α_A the basis set dependence is complicated by the 'frozen-core' approximation used for the atomic parameters and by the incorporation of a variational E_{val} .

A smaller α_A corresponds to a greater core penetrability of the valence orbital. This is clearly evident on comparing the $\alpha_{s,\text{Li}}$ with $\alpha_{s,\text{Na}}$ and $\alpha_{s,\text{Na}}$ with $\alpha_{p,\text{Na}}$. Furthermore, the last comparison is consistent with the radial probabilities near the nucleus associated with different l type orbitals.

The reduction in the number of fitting parameters when compared with other *ab initio* pseudopotential methods is particularly noticeable for the quasi-local operator. For example, in our formulation there is only a single fitting parameter for lithium ($\alpha_{s,\text{Li}}$) and two fitting parameters for sodium ($\alpha_{s,\text{Na}}$ and $\alpha_{p,\text{Na}}$). In contrast, in the latest formulation of Huzinaga *et al.* (1987), the 'purely' local operator requires the fitting of 16 and 18 parameters respectively, whereas the Pettersson *et al.* (1987) MO pseudopotential method requires 6 and 8 fitting parameters respectively.

4. Results and Discussion

The original VEOMP formulation (Nagy-Felsobuki and Peel 1978*a*, 1978*b*; Peel and von Nagy-Felsobuki 1987*a*, 1987*b*) was restricted to a minimum basis set, thereby severely limiting its effectiveness. In VALMOP this restriction is lifted and as a consequence more flexible basis sets can be used. Figs 1 and 2 superimpose the AE valence energy and eigenvalue of Li_2 respectively as a function of R with that of the corresponding VALMOP results for a variety of basis sets. The superimposition

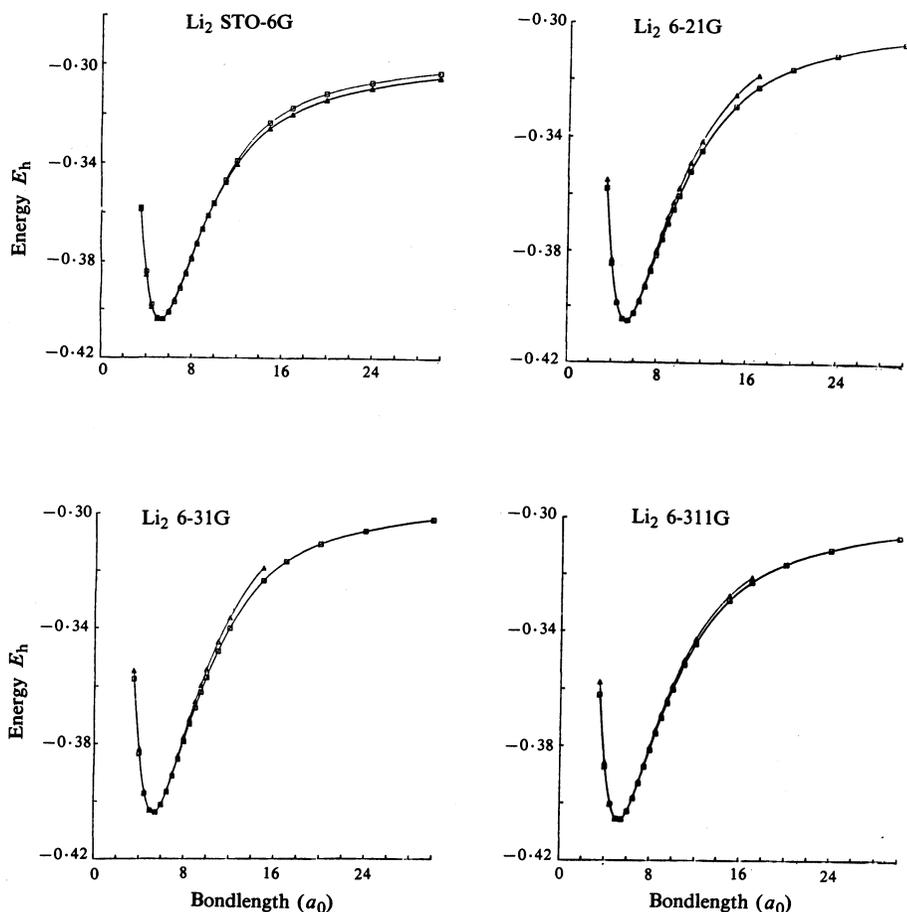


Fig. 1. Comparison of the Li_2 valence energy by VALMOP (triangles) and the reference all-electron calculations (squares) as a function of bondlength R for four different basis sets.

of the valence energies was achieved by calculating the valence energy of the AE calculations as

$$\Delta_{R_e} = \{E_h(\text{AE}) - E_h(\text{VALMOP})\}_{R_e}, \quad (7)$$

where the difference is at the AE equilibrium geometry; hence,

$$\text{Molecular valence } E_h(\text{AE})_R = E_h(\text{AE})_{R_e} - \Delta_{R_e}, \quad (8)$$

where the subscript R is the instantaneous bondlength. Equation (7) was determined at the respective minimum energy geometries and incorporated into equation (8) as a constant at all other geometries. At this geometry the pseudopotential valence eigenvalue was equated to the AE values.

For the STO-6G, 6-21G, 6-31G and 6-311G bases the standard deviations over R of the VALMOP energy/eigenvalue from the valence AE energy/eigenvalue are $0.0012E_h/0.0027E_h$, $0.0013E_h/0.0006E_h$, $0.0013E_h/0.0003E_h$ and

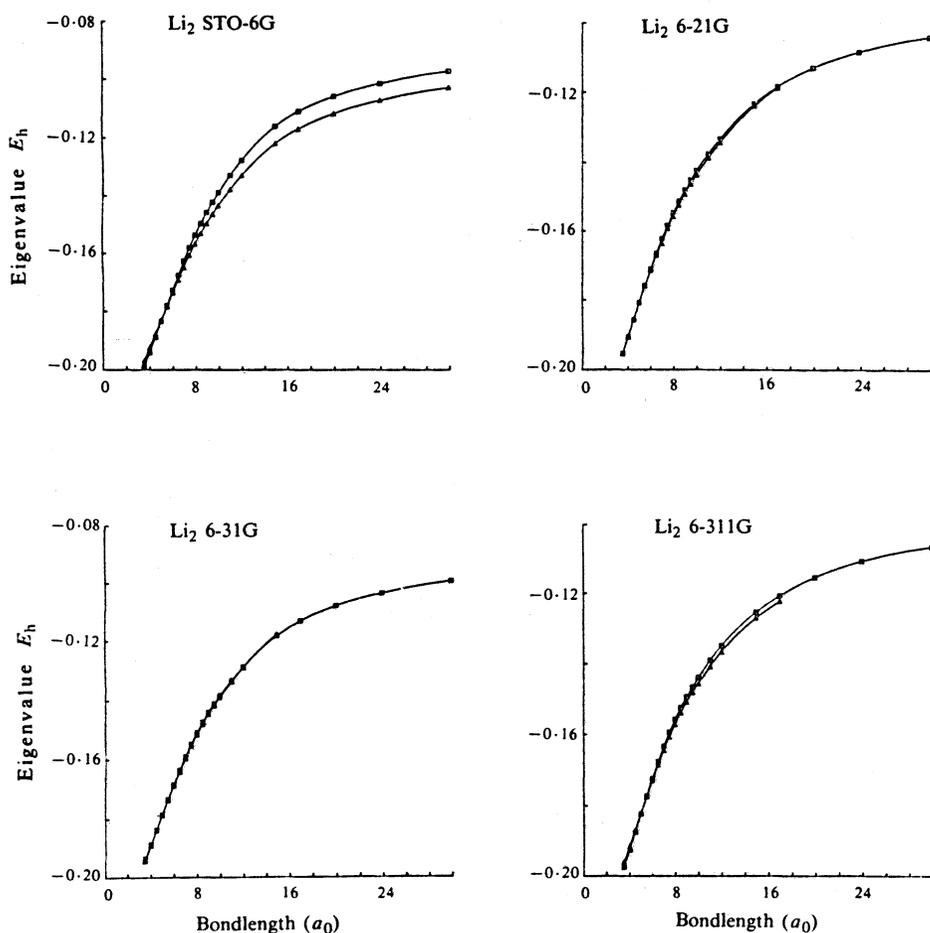


Fig. 2. Comparison of the Li_2 valence eigenvalue by VALMOP (triangles) and the reference all-electron calculations (squares) as a function of R for four different basis sets.

$0.0010 E_h / 0.0011 E_h$ respectively. Moreover, the predicted VALMOP/AE bondlengths are $5.224 a_0 / 5.302 a_0$, $5.316 a_0 / 5.320 a_0$, $5.328 a_0 / 5.320 a_0$ and $5.268 a_0 / 5.262 a_0$ respectively, with the differences in the predicted bondlength being $0.078 a_0$, $0.004 a_0$, $0.008 a_0$ and $0.006 a_0$ respectively. While for *ab initio* pseudopotential methods comparison with the reference AE calculation is of paramount importance, it should be noted that the experimental bond distance is $5.05 a_0$ (Huber and Herzberg 1979) and can only be accurately reproduced with large scale configuration interaction calculations.

While it is anticipated that because of the fitting procedure the comparison at the optimum *ab initio* bondlengths should be excellent, it is reassuring that this excellent agreement has been maintained at small R and to a lesser extent, at large R . For example, for the STO-6G, 6-21G, 6-31G and 6-311G basis sets the VALMOP/AE calculated vibrational frequencies are $349 \text{ cm}^{-1} / 332 \text{ cm}^{-1}$, $353 \text{ cm}^{-1} / 337 \text{ cm}^{-1}$, $351 \text{ cm}^{-1} / 338 \text{ cm}^{-1}$ and $344 \text{ cm}^{-1} / 334 \text{ cm}^{-1}$ respectively. This is of the same order of accuracy as achieved by Car and Martins (1981) where their pseudopotential/AE

comparison yielded $354 \text{ cm}^{-1}/340 \text{ cm}^{-1}$. The experimentally determined value is 351 cm^{-1} (Huber and Herzberg 1979), for which the pseudopotential results are fortuitously in better agreement than the AE calculations.

The agreement between VALMOP and the AE method does slightly degrade at large R due to the assumption that the quasi-local nature of the interpenetration term is largely independent of R . For example, for the STO-6G, 6-21G, 6-31G and 6-311G bases the absolute differences between the valence energy/eigenvalue for VALMOP and AE at $15a_0$ are $0.00234 E_h/0.00578 E_h$, $0.00392 E_h/0.00061 E_h$, $0.00436 E_h/0.00052 E_h$ and $0.00168 E_h/0.00165 E_h$ respectively.

The above agreement suggests that not only has the non-local nature of the interpenetration terms been effectively reproduced by VALMOP over a large range of R , but also that the pseudopotential term has effectively avoided the collapse of the valence orbital into assuming 'core-like' character. Furthermore, as anticipated the poorest results are given by the minimum basis set with the largest improvement being gained by increasing the flexibility of the split valence basis. That is, the improvement made from using a 6-21G over a STO-6G basis set far exceeds subsequent increases in the flexibilities of the valence basis sets.

In the case of Na_2 the need for a small but effective basis set is of paramount importance if the methodology is to be extended to the study of large sodium clusters. Hence, from our lithium results it is evident that the 6-21G basis set is a small and yet reliable flexible basis set (see Figs 1 and 2 and above). Consequently, we have restricted our study on Na_2 to the STO-6G and 6-21G basis sets.

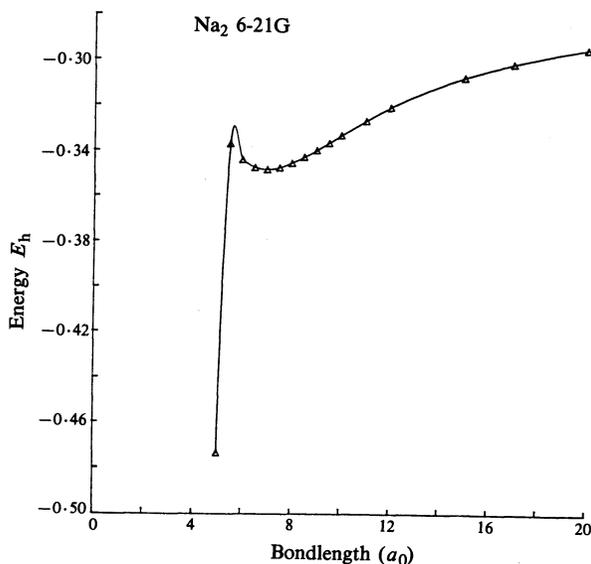


Fig. 3. VEOMP valence energy of Na_2 as a function of R showing a variational collapse at small R .

Fig. 3 demonstrates that for Na_2 and for the valence 21G basis set the VEOMP total energy suffers variational collapse into the inner core region. Fig. 4 gives the superimposition of the AE and VALMOP total valence energies as a function of R , whereas Fig. 5 shows the comparison between AE and VALMOP eigenvalues as

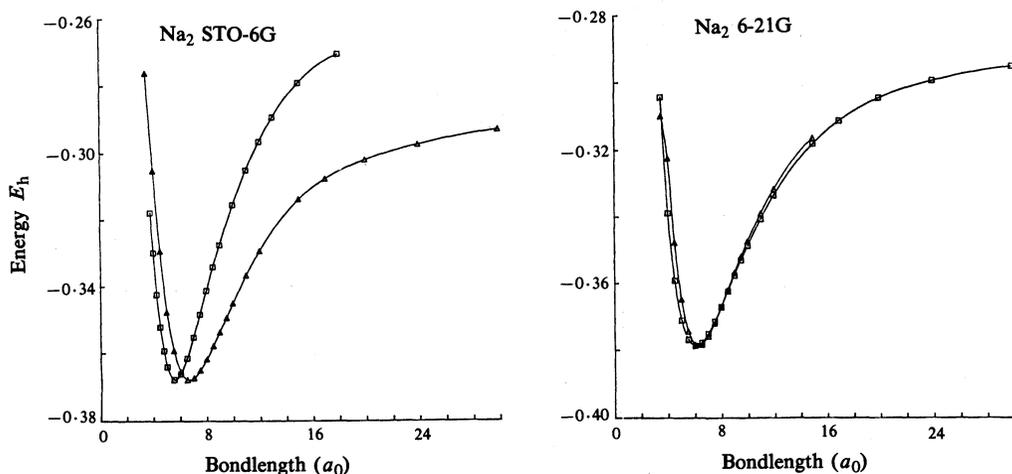


Fig. 4. Comparison of the Na₂ valence energy of VALMOP (triangles) and the reference all-electron calculations (squares) as a function of R for different basis sets.

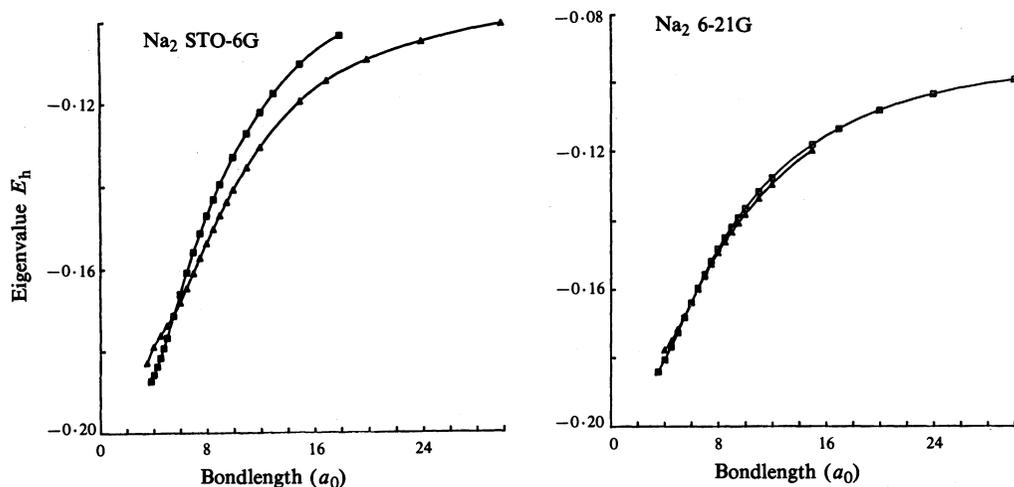


Fig. 5. Comparison of the Na₂ valence eigenvalue of VALMOP (triangles) and the reference all-electron calculations (squares) as a function of R for different basis sets.

a function of R . On comparing Figs 3 and 4 it is clear that the n, l flexibility of the interpenetration term of VALMOP (see equation 6) is the determining factor in preventing a variational collapse.

For the STO-6G and 6-21G bases the standard deviations of the VALMOP energy/eigenvalue from the valence AE energy/eigenvalue are $0.0207 E_h/0.0053 E_h$ and $0.0050 E_h/0.0014 E_h$ respectively. Moreover, the predicted VALMOP/AE bondlengths are $6.674 a_0/5.561 a_0$ and $6.246 a_0/6.047 a_0$ respectively, with the differences being $1.113 a_0$ and $0.199 a_0$ respectively. The experimental value is $5.82 a_0$ (Huber and Herzberg 1979). Once again the 6-21G results are almost an order of magnitude better than the corresponding STO-6G results, and when compared with the lithium 6-21G results are an order of magnitude poorer in agreement.

Interestingly, for Na_2 the shape of the VALMOP 6-21G potential curve more closely resembles that of the AE potential energy curve at large R and yet is poorer at small R : both effects can be rationalised because of the use of the 'frozen-core' approximation in VALMOP. So at small distances the approximation would be expected to be poor because of the polarisability of the sodium core in the molecular environment, whereas for large R this approximation would not be as pronounced. Hence, at $15a_0$ the absolute differences between the VALMOP and AE energy/eigenvalue is $0.00182 E_h/0.00154 E_h$, which compares favourably with the Li_2 result. Furthermore, the STO-6G and 6-21G VALMOP/AE calculated vibrational frequencies are $150 \text{ cm}^{-1}/214 \text{ cm}^{-1}$ and $169 \text{ cm}^{-1}/155 \text{ cm}^{-1}$ respectively. It is clear that only the larger basis set gives the same order of accuracy as achieved by Car and Martins (1981) as their pseudopotential/AE comparison yielded $163 \text{ cm}^{-1}/160 \text{ cm}^{-1}$. The experimental value is 159 cm^{-1} (Huber and Herzberg 1979).

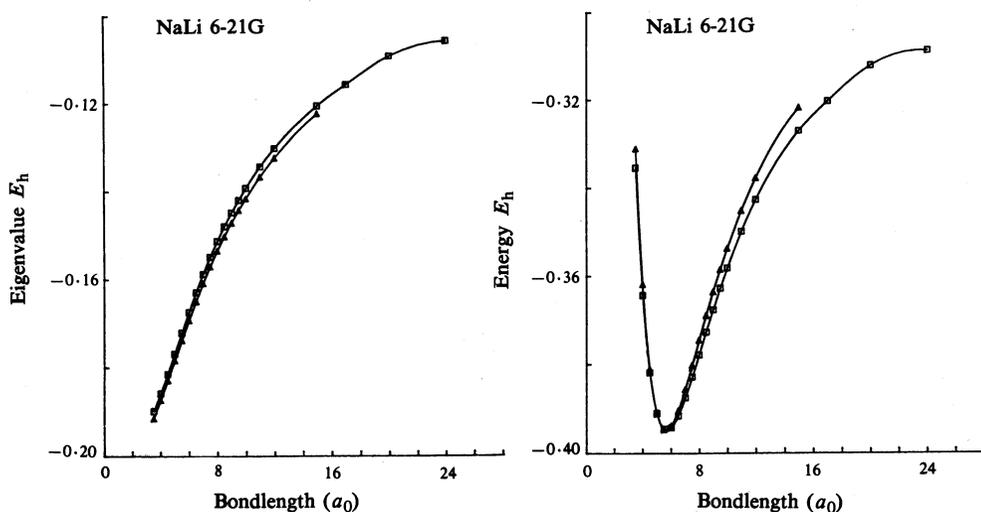


Fig. 6. Comparison of the NaLi valence eigenvalue and energy of VALMOP (triangles) and the reference all-electron calculations (squares) as a function of R .

An effective test of the VALMOP HF MO method is the electronic structure of NaLi, since for this diatomic molecule the VALMOP parameters have been previously determined and so are not optimised for this molecular case. Fig. 6 gives the superimposition of the AE and VALMOP total valence energies and eigenvalues as functions of R . The agreement between VALMOP and its AE reference calculations is excellent. The standard deviations between these two calculations of the valence energy/eigenvalue in hartrees is $0.0018/0.0003$ respectively. Furthermore, the VALMOP/AE predicted bondlength is $5.628a_0/5.695a_0$, the difference being $0.067a_0$. Furthermore, the 6-21G VALMOP/AE calculated vibrational frequency is $271 \text{ cm}^{-1}/245 \text{ cm}^{-1}$, somewhat poorer in agreement. It is satisfying that the predicted dipole moments of VALMOP/AE at the *ab initio* bondlength are $0.5445D/0.5355D$, in excellent agreement.

While agreement between VALMOP and AE is excellent for these diatomic molecules, such comparisons would be futile if VALMOP did not achieve any

economy over the AE method. For Li_2 , Na_2 and NaLi the AE/VALMOP CPU times (in seconds) at the AE geometry on a VAX 8550 computer are 10.6/6.2, 25.4/8.03 and 24.3/11.4 respectively. Nevertheless, it should be noted that the AE code is that of GAUSSIAN 86, whereas VALMOP is based on the GAUSSIAN 76 integral package, and that such comparisons are also tempered by differences in the quality of the initial guess of the coefficient matrix in the SCF cycle.

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