

POTENTIAL ENERGY CURVES FOR DIATOMIC MOLECULES CALCULATED WITH NUMERICAL BASIS FUNCTIONS

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A computational scheme for molecules is presented for the evaluation of total energy properties such as potential energy curves and vibrational frequencies. The calculations are performed within the local density approximation utilizing the LCAO MO scheme with numerical basis functions, and multipole expansion of the molecular charge density is used to obtain the molecular potential. The total energy expression is written in terms of matrix elements already used for solving one-electron equations, and hence any evaluation of explicit integrals over charge density is avoided. The accuracy of the method and the effect of basis set incompleteness are studied for the CO and N₂ molecules and compared with fully numerical (basis-free) results.

1. Introduction

During the last years a number of computational schemes within the local density approximation (LDA) [1–4] or $X\alpha$ [5] method have been developed for the evaluation of the total energy of molecular systems. Special interest has been focused on such properties as potential energy curves, dissociation energies and vibrational frequencies of diatomic molecules. This is partly because of the access to experimental data and their relative simplicity as a test ground for new methods before application to more complicated systems. Reviews of different calculations, methods and results have been presented by Delley and Ellis [6], Becke [7] and recently by Sundholm [8].

The objective has been to develop methods within LDA with a careful and accurate treatment of the molecular charge density and potential. The self-consistent procedures involve methods for solving the one-electron equations in the effective potential, which determine the charge density, and methods for solving the Poisson equation of the charge density, which gives the potential. The

critical point in the latest developments has been the application of different solution procedures to solve the Poisson equation. A choice of analytic basis functions reduces much of the effort, but at the cost of accuracy or basis size, whereas the use of more flexible numerical basis functions meets with difficulties in the numerical solution of the Poisson equation. These two alternatives are in standard use in linear combination of atomic orbitals (LCAO)-type methods, which are general methods used to evaluate the total energy in an accurate way. Fortunately, some fully numerical calculations, i.e. without any use of basis sets, are available [7–9] for the first-row diatomics and can be used as benchmarks of the $X\alpha$ or Hartree–Fock–Slater (HFS) limit.

Most of the LCAO molecular calculations done today are performed with Slater-type orbitals (STOs) or gaussian-type orbitals (GTOs) determined by energy optimization for the constituent atoms within Hartree–Fock (HF) or LDA methods. Often these STO and GTO basis sets tend to be rather extensive, when highly accurate results are required, and will probably limit the calculations to not too big systems. Extensive analysis of STO basis set effects on the electron density and spectroscopic constants for the CO

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molecule have recently been done by Baerends et al. [10]. Another approach is the use of linear combination of muffin-tin orbitals (LCMTO), by Gunnarsson, Harris and Jones [11], and later developments by Harris and Painter [12] and Müller et al. [13].

A quite different approach is to use numerical atomic-like wavefunctions, "single site orbitals", directly as basis functions in the construction of LCAO wavefunctions [14]. These numerical basis sets can be considered to be highly efficient contracted basis with the possibility to treat even very large molecular systems such as metal surfaces [15–17], metal clusters [18,19], or metal porphyrins [20,21]. Further, the Fock and overlap matrix elements are then evaluated with some numerical integration method. One of the most commonly used procedures is the discrete variational method (DVM) which in principle introduces no restrictions on the molecular potential [22].

The molecular potential in these methods can be calculated from Mulliken analysis of the molecular charge density leading to spherically overlapping atomic charge densities and Coulomb potentials as used in the self-consistent charge (SCC) method [23]. In a more accurate description of the molecular potential as achieved in the SCM method [6], multicenter–multipolar fitting functions can be used in addition to the SCC-like charge density.

The drawback left in these calculations is the DVM integration procedure which is adequate for evaluation of one-electron properties but suffers in numerical noise in the evaluation of total energy properties such as dissociation energies and vibrational frequencies. However, some of this noise can be eliminated by use of a Gauss–Legendre integration scheme [24] in spheres around each atom in the molecule and the use of the DVM integration procedure in the remaining regions only. Another approach for diatomic molecules is to use numerical basis sets and solve the Poisson equation fully numerically as done by Sepp et al. [25].

We present in this work our method for the total energy calculation of molecular systems. Some results are presented on the evaluation of potential energy curves, dissociation energies and

vibrational frequencies for the diatomic molecules CO and N₂ with an emphasis on investigation of basis sets effects and noise from the DVM method. A short review of the calculation procedure is presented in section 2 with the results and discussions in section 3 and, finally, summary and conclusions in section 4.

2. Calculation procedures

2.1. One-electron equation

To evaluate the ground-state properties of a many-electron system the Schrödinger equation is reduced to one-electron equations within the density functional theory formulated by Hohenberg, Kohn and Sham [1,2]. In the LDA [1–4] the one-electron hamiltonian in atomic units is

$$h(\mathbf{r}) = -\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}), \quad (1)$$

where the first term on the right-hand side represents the kinetic energy operator (later referred to as t) of an electron in the effective potential $v_{\text{eff}}(\mathbf{r})$. This is written as

$$v_{\text{eff}}(\mathbf{r}) = -\sum_{\nu} \frac{Z_{\nu}}{|\mathbf{r} - \mathbf{R}_{\nu}|} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}(\rho(\mathbf{r})), \quad (2)$$

where the first term is the nuclear Coulomb potential $v_n(\mathbf{r})$ of the nuclei ν with charges Z_{ν} at positions $\mathbf{R}_{\nu}$, the second term is the electronic Coulomb potential $v_e(\mathbf{r})$ of the molecular charge density $\rho(\mathbf{r})$, and the last term stands for the remaining electron–electron interactions, i.e. for the exchange and correlation contributions.

To calculate the molecular electron structure we use the LCAO procedure and expand the one-electron orbitals as

$$\Psi_i(\mathbf{r}) = \sum_j \chi_j(\mathbf{r}) c_{ji}, \quad (3)$$

in terms of expansion coefficients c_{ji} , i.e. eigenvectors c_i and symmetry functions $\chi_j(\mathbf{r})$. These symmetry functions are composed of, for example, free atom and/or free ion radial wavefunctions $u_{nl}(r)$ in numerical form and the spherical

harmonics $Y_{lm}(\hat{\mathbf{r}})$ as

$$\chi_j(\mathbf{r}) = \sum_{nlm} W_{nlm}^{j\nu} u_{nl}(r_\nu) Y_{lm}(\hat{\mathbf{r}}_\nu). \quad (4)$$

The coefficients W are chosen to generate basis functions χ_j , which transform according to the irreducible representations of the point group of the hamiltonian. Using these basis functions it is convenient to write the Schrödinger equation corresponding to the hamiltonian of eq. (1) in an equivalent matrix form

$$\mathbf{H}\mathbf{c}_i = \epsilon_i \mathbf{S}\mathbf{c}_i, \quad (5)$$

with the matrix elements for the hamiltonian $\mathbf{H}$ and overlap matrices $\mathbf{S}$ as

$$H_{kl} = \int \chi_k^*(\mathbf{r}) h(\mathbf{r}) \chi_l(\mathbf{r}) d\mathbf{r} = \langle k | h | l \rangle \quad (6)$$

and

$$S_{kl} = \int \chi_k^*(\mathbf{r}) \chi_l(\mathbf{r}) d\mathbf{r} = \langle k | l \rangle, \quad (7)$$

which lead to a block form of matrices reducing the efforts for numerical diagonalization.

To obtain matrix elements H_{kl} for the hamiltonian, a decomposition according to the eqs. (1) and (2) is made and the contributions are evaluated as follows. The kinetic energies of the atomic and ionic wavefunctions $u_{nl}(r)$ are used together with eq. (4) to compute the matrix elements for the kinetic energy

$$T_{kl} = \langle k | t | l \rangle. \quad (8)$$

The molecular charge density, explicit in eq. (2), is obtained from the one-electron solutions eq. (3) and their occupation numbers q_i as

$$\rho(\mathbf{r}) = \sum_i q_i |\Psi_i(\mathbf{r})|^2 \quad (9)$$

$$= \sum_i q_i \sum_{kl} \chi_k^*(\mathbf{r}) \chi_l(\mathbf{r}) c_{ki}^* c_{li}. \quad (10)$$

The multipole expansion technique SCM [6] is then used to solve the electronic potential $v_e(\mathbf{r})$ in an explicit form. The true molecular charge density of eq. (9) is approximated with a model charge density constructed as

$$\rho_{\text{model}}(\mathbf{r}) = \sum_{\nu,i} n_i \rho_i^*(\mathbf{r}) + \sum_j n_j \rho_j(\mathbf{r}), \quad (11)$$

where $\rho_i^*(\mathbf{r}) = |u_{ni}(r_\nu)|^2$ are spherical charge densities from atomic radial wavefunctions at sites ν . $\rho_j(\mathbf{r})$ are multipole functions, which allow analytic integration and are chosen according to the fully symmetric representation of the relevant point group. The “occupation numbers” n_i and n_j are simultaneously determined in a least-squares fit by minimizing the integral

$$\Delta = \int [\rho(\mathbf{r}) - \rho_{\text{model}}(\mathbf{r})]^2 d\mathbf{r}. \quad (12)$$

If the second sum in eq. (11) is neglected, the occupations n_i of atomic orbitals $u_{ni}(r_\nu)$ may be evaluated using Mulliken analysis as done in the SCC approximation [23], which leads to a superposition of spherical charges and corresponding Coulomb potentials.

Now the matrix elements for all three contributions to $v_{\text{eff}}(\mathbf{r})$ in eq. (2) can be computed provided that some explicit form for $v_{\text{xc}}(\rho)$ is chosen. Finally the matrix equation (5) is solved self-consistently for eigenvectors $\mathbf{c}_i$ and eigenvalues ϵ_i .

2.2. Total energy

The total energy for the molecule can be written using the previous notations as

$$E = T + \int \rho(\mathbf{r}) v_n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \rho(\mathbf{r}) v_e(\mathbf{r}) d\mathbf{r} + E_{\text{xc}} + E_{\text{nuc}}, \quad (13)$$

where T is the kinetic energy, v_n and v_e represent one-electron effective potentials for electron-nuclei and electron-electron interactions, E_{xc} is the exchange-correlation energy and the last term stands for the internuclear repulsion energy,

$$E_{\text{nuc}} = \sum_{\substack{\mu, \nu \\ \mu < \nu}} \frac{Z_\mu Z_\nu}{|\mathbf{R}_\mu - \mathbf{R}_\nu|}. \quad (14)$$

In our procedure we can write the Coulomb integrals in eq. (13) conveniently in terms of corresponding matrix elements, already used in solving the one-electron equations, and hence avoid explicit integration procedures with additional numerical errors. First we write the charge density

of eq. (10) in a form

$$\rho(\mathbf{r}) = \sum_{kl} \chi_k^*(\mathbf{r}) \chi_l(\mathbf{r}) \rho_{kl}, \quad (15)$$

where

$$\rho_{kl} = \sum_i q_i c_{ki}^* c_{li}. \quad (16)$$

Then we can write the electronic potential energy in the nuclear Coulomb field in eq. (13) as

$$\begin{aligned} V_n &= \int \rho(\mathbf{r}) v_n(\mathbf{r}) d\mathbf{r} = \sum_{kl} \rho_{kl} \int \chi_k^*(\mathbf{r}) v_n(\mathbf{r}) \chi_l(\mathbf{r}) \\ &= \sum_{kl} \rho_{kl} \langle k | v_n | l \rangle \end{aligned} \quad (17)$$

and the electron–electron Coulomb energy in eq. (13) as

$$\frac{1}{2} V_e = \frac{1}{2} \int \rho(\mathbf{r}) v_e(\mathbf{r}) d\mathbf{r} = \frac{1}{2} \sum_{kl} \rho_{kl} \langle k | v_e | l \rangle. \quad (18)$$

Referring to eqs. (1) and (2) we can also formally write the quantities

$$V_{\text{eff}} = \sum_{kl} \rho_{kl} \langle k | v_{\text{eff}} | l \rangle, \quad (19)$$

$$V_{\text{xc}} = \sum_{kl} \rho_{kl} \langle k | v_{\text{xc}} | l \rangle, \quad (20)$$

and analogously for the kinetic energy from eq. (8)

$$T = \sum_{kl} \rho_{kl} T_{kl}. \quad (21)$$

The alternative way of writing the kinetic energy is to solve eq. (1) for non-interacting electrons and sum over all levels i to obtain

$$T = \sum_i q_i \epsilon_i - V_{\text{eff}}, \quad (22)$$

which in our procedure is even numerically equivalent with eq. (21), since any explicit numerical integrations are not required. Finally we write for the exchange–correlation energy analogously,

$$E_{\text{xc}} = \int \rho(\mathbf{r}) \epsilon_{\text{xc}}(\rho(\mathbf{r})) d\mathbf{r} = \sum_{kl} \rho_{kl} \langle k | \epsilon_{\text{xc}} | l \rangle, \quad (23)$$

where any LDA functional for energy per electron

$\epsilon_{\text{xc}}(\rho)$ may be used. This leads finally to a total energy expression

$$E = \sum_i q_i \epsilon_i - \frac{1}{2} V_e - V_{\text{xc}} + E_{\text{xc}} + E_{\text{nuc}}. \quad (24)$$

It should be noted that eq. (24) represents the general expression for the total energy within the LDA. In practical calculations however, different types of LDA may be applied.

The Hartree–Fock–Slater or $X\alpha$ method [5] is based on the local-density approximation of the form

$$v_{\text{xc}}(\rho(\mathbf{r})) = -3\alpha \left(\frac{3}{8} \rho(\mathbf{r}) / \pi \right)^{1/3}, \quad (25)$$

where the parameter α can be chosen within certain limits but is usually fixed to $\alpha = 0.7$. The simple charge density dependence $v_{\text{xc}} \propto \rho^{1/3}$ in $X\alpha$ implies that

$$E_{\text{xc}} = \frac{3}{4} V_{\text{xc}}, \quad (26)$$

and we obtain a simple form for the total energy within the $X\alpha$ scheme

$$E = \sum_i q_i \epsilon_i - \frac{1}{2} V_e - \frac{1}{4} V_{\text{xc}} + E_{\text{nuc}}. \quad (27)$$

We want to emphasize that all of the contributions to total energy in eq. (13) can be evaluated without explicit numerical integrations, except those needed to solve the one-electron equations. We expect therefore our procedure to be accurate within the SCF LCAO method. The drawback is, however, that all of the electrons have to be treated explicitly, and for heavy elements the useful frozen core procedure inevitably leads to additional approximations, whereas the method of Delley et al. [18,26] employing direct integration is more flexible in this sense.

3. Results and discussion

As a test of our approach for the total energy calculation and related quantities such as potential energy curves, dissociation energies, bond lengths and vibration frequencies, calculations were performed for CO and N₂ for which there exist a number of different $X\alpha$ calculations to compare with. Of particular interest is the recent analysis of

Table 1

The atoms, ions and the consequent orbitals $u_{nl}(r)$ which are used to generate the basis functions

Molecule	Basis set	Atomic orbitals
CO	DB	C(1s,2s,2p) C^{2+} (2s*,2p*) O(1s,2s,2p) O^{2+} (2s*,2p*)
	DBD	C(1s,2s,2p) C^{2+} (2s*,2p*,3d*) O(1s,2s,2p) O^{4+} (2s*,2p*,3d*)
N ₂	DB	N(1s,2s,2p) N^{3+} (2s*,2p*)
	DBD	N(1s,2s,2p) N^{3+} (2s*,2p*,3d*)
	DBDF	N(1s,2s,2p) N^{3+} (2s*,2p*,3d*,4f*)

basis set effects by Baerends et al. [10] for the CO molecule. A comparison is done for both CO and N₂, with the fully numerical result of Becke [7] and Laaksonen et al. [9]. Finally, a comparison is also done with results using GTO basis sets by Dunlap et al. [27]. The accuracy of our calculations appears to be mainly determined by the completeness of the basis set, the goodness of the fit to the molecular charge density and the numerical noise inherent in the numerical integration procedure.

3.1. Basis sets

The different basis function sets used in the calculations are described in tables 1 and 2. The radial parts of the atomic wavefunctions are calculated with an atomic X α code with the exchange parameter $\alpha = 0.7$ and the basis set is then composed of different combinations of functions according to eq. (4). The wavefunctions of the

ionized atoms are calculated for the particular ion and only the outermost occupied and virtual orbitals are included as basis functions. The degree of ionicity should be sufficient to create a flexible basis but otherwise it is not critical.

The smallest basis of those presented, referred as DB, is composed of the basis of the neutral atom with additional s and p orbitals from an ionized atom of each type. In the larger basis sets DBD and DBDF d and f orbitals are also included.

3.2. Numerical procedure

Calculations of total energy including dissociation energies, vibrational frequencies and bond lengths require a good description of the molecular charge density $\rho(r)$ for evaluation of $v_{\text{eff}}(r)$. The SCC superposition of spherical charges gives a description of the charge density which is too poor for that purpose, although the transition state energies are in rather good agreement with experimental values [23]. However, the multipole expansion of the true molecular charge $\rho(r)$ to the model charge density $\rho_{\text{model}}(r)$ instead, seems to be an efficient and accurate procedure.

Evaluation of the matrix elements and hence also the total energy is based on the DVM method developed by Ellis and co-workers [14,22,28]. This procedure originates from the Diophantine integration scheme by Haselgrove [29] and Conroy [30]. The advantage is that no specific restrictions are imposed on the molecular potential but a large number of sampling points are required for accurate results. The error is proportional to N^{-1} ,

Table 2

Energy eigenvalues in atomic units for the free atom and free ion wavefunctions given in table 1

	Carbon atom	Oxygen atom	Nitrogen atom	
1s	-9.956	-18.785	-14.029	
2s	-0.471	-0.840	-0.645	
2p	-0.169	-0.306	-0.235	
	Carbon C^{2+}	Oxygen O^{2+}	Oxygen O^{4+}	Nitrogen N^{3+}
2s*	-1.442	-2.097	-3.722	-2.456
2p*	-1.136	-1.559	-3.246	-2.064
3d*	-0.282		-1.060	-0.614
4f*				-0.291

where N is the number of points in the integration formula. Sampling of the points $D(\mathbf{r})$ are usually taken as a sum of spherical Fermi–Dirac distributions centered at different atoms in the molecule [14]

$$D(\mathbf{r}) = \sum_{\nu} t_{\nu} d_{\nu}(\mathbf{r}),$$

where

$$d_{\nu}(\mathbf{r}) \propto \{r^2 \{1 + \exp[\beta_{\nu}(r - R_0^{\nu})]\}\}^{-1} \quad (28)$$

and t_{ν} is an adjustable sampling weight.

In order to overcome the shortcomings with the DVM integration, a Gauss–Legendre-type of integration is used inside non-overlapping spheres surrounding the nuclei and DVM integration is used outside the spheres. A uniform point distribution is achieved when varying the internuclear distance by scaling the parameter R_0^{ν} with this distance while keeping $\beta_{\nu} R_0^{\nu}$ constant. This approach gives a comparatively small integration error when calculating the bond length.

The dissociation energy is obtained from

$$D_e = |E_{\text{mol}}(a, b) - E_{\text{atom}}(a) - E_{\text{atom}}(b)|, \quad (29)$$

where the atomic energies $E_{\text{atom}}(i)$ are computed with the molecular code and the same integration mesh. It is then possible to estimate the numerical error by varying the number of integration points and using the atomic energies as reference values.

Table 3

Properties of CO as a function of basis type. A comparison with some other results from Baerends et al [10], the basis-free calculations of Laaksonen [9] and Becke [7] and the GTO results from Dunlap et al. [27]

	r_e (bohr)	ω_e (cm ⁻¹)	D_e (eV)
DB	2.130	2512	11.11
DBD	2.14	2475	11.27
DZ [10]	2.175	2003	10.196
QZ [10]	2.177	2012	10.502
QZDDF [10]	2.132	2173	11.966
L [9]	2.128	2174	12.084
B [7]	2.13	2170	12.0
DCS [27]	2.132	2160	11.98
exp. [31]	2.132	2170	11.2

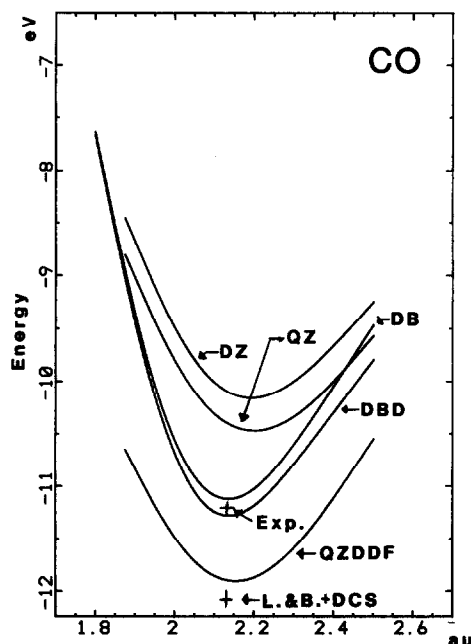


Fig. 1. Potential energy curves for CO with different basis sets. See table 3 for notations.

3.3. Results

Tables 3 and 4 show the dissociation energies D_e , bond lengths, r_e , and vibrational frequencies, ω_e , for CO and N₂. The vibrational frequency, ω_e , and bond length, r_e , were determined by fitting a Morse potential to our results at eight different distances in the vicinity of the equilibrium distance. As a comparison the experimental values are included. The potential curves are shown in figs. 1 and 2. The orbital energies from our calculations compared to the fully numerical result of

Table 4

Properties of N₂ as a function of basis type

	r_e (bohr)	ω_e (cm ⁻¹)	D_e (eV)
DB	2.11	2207	7.33
DBD	2.10	2375	9.01
DBDF	2.05	2396	9.30
L [9]	2.067	2393	9.6095
B [7]	2.07	2380	9.6
DCS [27]	2.074	2370	9.2
exp. [31]	2.07	2358	9.9

Table 5

Orbital energies in atomic units for CO and N₂. Internuclear distance $r = 2.13$ au for CO and $r = 2.07$ au for N₂

	$\epsilon(1\sigma)$	$\epsilon(2\sigma)$	$\epsilon(3\sigma)$	$\epsilon(4\sigma)$	$\epsilon(1\pi)$	$\epsilon(5\sigma)$
CODB ^{a)}	-18.7543	-9.9391	-1.0991	-0.4861	-0.4268	-0.3016
CODBD ^{a)}	-18.7490	-9.9343	-1.0653	-0.4955	-0.4170	-0.2972
L ^{b)}	-18.744119	-9.911357	-1.044174	-0.489074	-0.412614	-0.303031
	$\epsilon(1\sigma_g)$	$\epsilon(1\sigma_u)$	$\epsilon(2\sigma_g)$	$\epsilon(2\sigma_u)$	$\epsilon(1\pi_u)$	$\epsilon(3\sigma_g)$
NDB ^{a)}	-13.9979	-13.9962	-1.0817	-0.4555	-0.4252	-0.3482
NDBD ^{a)}	-13.9946	-13.9930	-1.0443	-0.4634	-0.4162	-0.3572
NDBDF ^{a)}	-13.9935	-13.9921	-1.0390	-0.4616	-0.4138	-0.3546
L ^{b)}	-13.981070	-13.979661	-1.007215	-0.460725	-0.404235	-0.350058

^{a)} Present work. ^{b)} Ref. [9].

Laaksonen et al. are given in table 5. We notice how the extension of the basis gives a better agreement with the eigenvalues obtained in the pure numerical calculations and with the potential energy curves calculated by Baerends et al. [10] with the extended basis set.

As pointed out before, for example by Becke [7], there is a good agreement between experiment

and LDA method for dissociation energies, vibrational frequencies and bond lengths. The 3d basis functions appear to improve the dissociation energy of N₂ remarkably but have less effect on that of CO, whereas the 4f basis functions are important to achieve the correct bond length of N₂. Due to numerical problems we did not succeed in using 4f functions for CO. The dissociation energies and bond lengths are however, in reasonable agreement for both of the molecules compared to fully numerical and experimental results. Also the vibrational frequency of N₂ is in good agreement but that of CO is not quite satisfactory. The reason for that might be either in the lack of 4f functions or in the numerical procedure, where the scaling of integration mesh causes a slow change in the DVM integration error.

4. Conclusions

Our numerical basis functions are in no way optimized but despite of that it is possible to get rather close to the properties evaluated with the basis-free methods. Our code is a general one for treating molecules of different size and geometry and we cannot derive a benefit from the choice of coordinate system compared to some of the other reported calculations. The use of numerical basis functions seems to be rather efficient also for treating total energy properties. We therefore expect our method to be efficient for large and complicated systems, too.

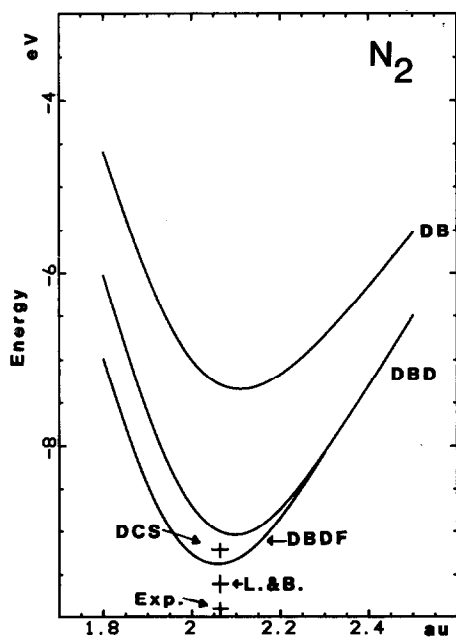


Fig. 2. Potential energy curves for N₂ with different basis sets. See table 4 for notations.

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