

Completely numerical calculations on diatomic molecules in the local-density approximation

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We have carried out completely numerical molecular-orbital calculations (i.e., no linear-combination-of-atomic-orbitals basis sets or cellular approximations) on 13 first- and second-row dimers from H_2 to Cl_2 in the local-density approximation. The resulting ground-state bond lengths, dissociation energies, and vibrational frequencies are reported and compared with experimental values.

Recent density-functional calculations on the transition-metal dimers Cr_2 and Mo_2 strongly recommend the local-density approximation (LDA) for exchange-correlation energy in molecular and solid-state systems.¹⁻³ The LDA, in combination with an "antiferromagnetic" relaxation of spin symmetry, gives excellent bond lengths and vibrational frequencies in these transition-metal systems, and reasonable dissociation energies as well. On the other hand, the popular $X\alpha$ exchange-only approximation⁴ gives very much poorer results. Therefore, we feel that a systematic survey of the local-density approximation in molecular systems is called for.

The most extensive study so far of the LDA in small molecular systems has been carried out by Painter and Averill⁵ on the first-row molecules H_2 through F_2 . These authors use a Gaussian-type-orbital (GTO) basis-set method which gives fairly accurate spectroscopic properties. Their method is somewhat similar to the GTO- $X\alpha$ scheme of Dunlap, Connolly, and Sabin^{6,7} and gives comparable results. However, an equally complete survey of second-row LDA molecular properties has not, as yet, been published, so we have undertaken to do so in the present work. Further, we use a completely numerical computational scheme [i.e., no linear-combination-of-atomic-orbitals (LCAO) basis sets or cellular approximations of any kind] which eliminates the basis-set errors inherent in the traditional LCAO methods.

The first completely numerical self-consistent computations on molecular systems were performed by the present author on first-row diatomic molecules in the $X\alpha$ approximation.⁸⁻¹⁰ A similar numerical scheme has also been developed by Pyykkö and co-workers with applications to a wide variety of molecular-orbital theories such as Hartree-Fock, $X\alpha$, multiconfiguration self-consistent-field and Dirac-Slater theories.^{11,12} In the present work, the numerical code of Becke⁸⁻¹⁰ is used to compute the ground-state bond lengths, bond energies, and vibrational frequencies of 13 first- and second-row dimers from H_2 to Cl_2 in the local-density approximation. These calculations comprise, to the best of our knowledge, the first completely numerical self-consistent computations of any kind on second-row diatomic systems (although Pyykkö's group has recently completed a spin-restricted numerical $X\alpha$ calculation on the Cr_2 dimer¹³).

In the density-functional formalism of Hohenberg, Kohn, and Sham^{14,15} the total electronic energy of an N -electron system is given by (in a.u.)

$$E = \frac{1}{2} \sum_{i=1}^N \int |\nabla\psi_i|^2 d^3\mathbf{r} + \int \rho V_{\text{ext}} d^3\mathbf{r} + \frac{1}{2} \int \int \frac{\rho(1)\rho(2)}{r_{12}} d^3\mathbf{r}_1 d^3\mathbf{r}_2 + E_{\text{xc}}(\rho\uparrow, \rho\downarrow),$$

where the ψ_i are integrally occupied single-particle orbitals, ρ is the total electron density,

$$\rho = \sum_{i=1}^N |\psi_i|^2,$$

V_{ext} is the Coulomb potential due to the atomic nuclei, and the last term E_{xc} is known as the exchange-correlation energy. It can be shown¹⁴ that the exchange-correlation energy is a unique functional of the spin densities $\rho\uparrow$ and $\rho\downarrow$.

In the local-density approximation (LDA) the exchange-correlation energy is estimated as follows:

$$E_{\text{xc}}^{\text{LDA}} = \int \rho \epsilon_{\text{xc}}(\rho\uparrow, \rho\downarrow) d^3\mathbf{r},$$

where ϵ_{xc} is the exchange-correlation energy per particle of a uniform electron gas with spin-up and spin-down electron densities given by the local values of $\rho\uparrow$ and $\rho\downarrow$, respectively. In the present calculations, we use for $\epsilon_{\text{xc}}(\rho\uparrow, \rho\downarrow)$ the electron-gas Monte Carlo data of Ceperley and Alder¹⁶ as parametrized by Vosko, Wilk, and Nusair.¹⁷

The following so-called Kohn-Sham equation for the single-particle orbitals ψ_i is obtained by applying the variational principle to the above total energy:

$$-\frac{1}{2} \nabla^2 \psi_i + (V_{\text{ext}} + V_{\text{el}} + V_{\text{xc}}^\sigma) \psi_i = \epsilon_i \psi_i,$$

where V_{el} is the Coulomb potential arising from the total electron density,

$$V_{\text{el}}(1) = \int \frac{\rho(2)}{r_{12}} d^3\mathbf{r}_2,$$

and V_{xc}^σ is the exchange-correlation potential given by the functional derivative of E_{xc} ,

$$V_{\text{xc}}^\sigma = \frac{\delta E_{\text{xc}}}{\delta \rho_\sigma}.$$

In the local-density approximation, this functional derivative is simply

$$V_{xc}^{\sigma}(\text{LDA}) = \frac{\partial}{\partial \rho_{\sigma}} [\rho \epsilon_{xc}(\rho \uparrow, \rho \downarrow)].$$

Notice that the exchange-correlation potential is spin dependent, which is important in the present context because we deal with spin-polarized separated atoms and some molecular triplet states as well. Our calculations are therefore completely spin unrestricted (i.e., we use different exchange-correlation potentials for spin “up” and spin “down” electrons in spin-polarized systems).

We solve the Kohn-Sham equation for the single-particle orbitals ψ_i and also the Poisson equation for the Coulomb potential V_{el} using the completely numerical code described in Refs. 8–10. All functions are defined on a discrete two-dimensional mesh in prolate spheroidal coordinates (related to the elliptical coordinates familiar to chemists) and all necessary integrations and differentiations on this mesh are carried out using two-dimensional cubic spline analysis. This approach has the obvious advantage over the usual basis-set schemes, that numerical accuracy is easily controlled by adjusting the number of mesh points.

In the present calculations, we have used three meshes containing 14×22 , 20×32 , and 30×48 points (notation of Ref. 8) or a total of 308, 640, and 1440 points, respectively. Even for the second-row systems dealt with here, the difference in bond energies between the 308- and the 1440-point calculations is typically only a few hundredths of an electron volt. The corresponding typical difference in bond lengths is less than 0.01 bohr, and for the vibrational frequencies it is less than 10 cm^{-1} . In other words, our results show very satisfactory consistency over a four-fold increase in the total number of mesh points. Greater accuracy could, of course, be achieved (at substantially greater cost) by increasing the size of our meshes even further, but this level of precision is quite adequate for the present purposes.

In computing our dissociation energies, we use exactly the same numerical code and the same discrete mesh for both the molecular and the corresponding separated-atom

calculations in order to take advantage of the resulting cancellation of numerical errors. In this way, one obtains accurate spectroscopic properties even on relatively coarse meshes. It should be noted, however, that density-functional atomic energies have a slight dependence on M_L , the z component of total angular momentum. This is due to the fact that the degenerate complex spherical harmonic functions $Y_{LM}(\theta, \phi)$ do *not* have equivalent densities. In a fully two-dimensional calculation such as ours, this M_L dependence can only be eliminated by introducing fractional occupation numbers. In the present work, however, we restrict ourselves to *integral* occupation numbers and assume that $M_L = 0$ in all of our atomic calculations (see the Appendix of Ref. 18 for further discussion of this point).

The bond lengths and vibrational frequencies have been determined by fitting a cubic polynomial in *inverse* r to eight points in the vicinity of the equilibrium internuclear separation. This inverse- r fit was used in our previous $X\alpha$ calculations⁸ and is adopted from the work of Dunlap, Connolly, and Sabin.⁷

In Table I we present the LDA bond lengths r_e , bond energies D_e , and vibrational frequencies ω_e for our 13 first- and second-row dimers from H_2 to Cl_2 . The experimental ground-state symmetry is assumed in each case. As indicated above, the numerical accuracy of these results is 0.01 bohr, 0.1 eV, and 10 cm^{-1} , respectively, and the entries in Table I are therefore rounded appropriately. Also, we show the corresponding experimental results as compiled in Ref. 19.

In general, the LDA bond lengths and vibrational frequencies are remarkably good. The rms deviation from experiment for the 13 molecules in Table I is only 0.05 bohr for the bond lengths and 80 cm^{-1} for the vibrational frequencies. On the other hand, the LDA dissociation energies tend to be much too large, with an rms deviation from experiment of 1.2 eV. These general trends have already been observed by Painter and Averill⁵ and others in first-row systems and in the recent transition-metal calculations as well.^{1–3} The present work confirms that these trends hold for second-row systems also. Finally, we should mention that the first-row results of Painter and

TABLE I. LDA spectroscopic constants.

	r_e (bohrs)		D_e (eV)		ω_e (cm^{-1})	
	Expt.	LDA	Expt.	LDA	Expt.	LDA
H_2	1.40	1.45	4.8	4.9	4400	4190
Li_2	5.05	5.12	1.1	1.0	350	330
B_2	3.00	3.03	3.0	3.9	1050	1030
C_2	2.35	2.35	6.3	7.3	1860	1880
N_2	2.07	2.07	9.9	11.6	2360	2380
O_2	2.28	2.27	5.2	7.6	1580	1620
F_2	2.68	2.61	1.7	3.4	890	1060
Na_2	5.82	5.67	0.8	0.9	160	160
Al_2	4.66	4.64	1.8	2.0	350	350
Si_2	4.24	4.29	3.1	4.0	510	490
P_2	3.58	3.57	5.1	6.2	780	780
S_2	3.57	3.57	4.4	5.9	730	720
Cl_2	3.76	3.74	2.5	3.6	560	570

Averill agree reasonably well with the present completely numerical results.

These calculations constitute the most extensive examination to date of the local-density approximation in diatomic systems. We hope that our results will be of interest to workers in density-functional theory and in quantum chemistry. Having established numerically reliable LDA spectroscopic properties for first- and second-row

molecules, our challenge now is to improve the LDA results by considering nonlocal corrections such as that of Langreth and Mehl.²⁰ We are currently very interested in this problem and will publish our preliminary findings in the near future.

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