Theoret. Chim. Acta (Berl.) 63, 349–356 (1983)

THEORETICA CHIMICA ACTA

Wigner's Phase Space Function and the Bond in LiH

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Wigner's phase space function for LiH is calculated and compared with the function for the system consisting of two non-interacting Li and H atoms.

Key words: Wigner's phase space function – Chemical bond – LiH.

1. Introduction

In some recent papers [1–7] we have interpreted Wigner's phase space function as an electron density in the six dimensional phase space, and examined it for some simple atomic systems: the hydrogen atom [3], and the helium, the beryllium, the neon, the argon, and the zinc atom [5]. Those investigations represent, as far as we know, the only examination of the phase space function for atomic states, although it was introduced by Wigner as early as in 1932 [8].

The phase space function makes a very detailed study of atomic structure possible, e.g. including a possibility of comparing classical and quantum mechanics in a simple way. Therefore, it seems natural to extend our earlier analysis to molecular systems too. Hence, in this paper we present an investigation of the formation of the LiH molecule as seen from a phase space point of view. LiH is chosen since it is one of the smallest heteropolar molecules, and many theoretical investigations have been performed on this molecule (see e.g. [13–17]). It has been stated [16] that a Hartree–Fock wavefunction provides a reliable description of the chemical bond in LiH. Thus, in this paper we will not go beyond the Hartree–Fock wavefunction.

For details about the Wigner phase space function the reader is referred to [1–7] and references therein.

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2. Phase Space Functions for LiH

LiH can be described in a cartesian coordinate system with the Li nucleus placed at origo and the H nucleus placed at $(x, y, z) = (0, 0, R)$, where we here have chosen the experimental bond length [9]:

$$R = 3.015 \text{ a.u.} \tag{1}$$

We have here and anywhere else in this paper used atomic units, i.e. the electronic mass m_e and Planck's constant $\hbar$ are set to 1 and the electronic charge $-e$ to -1.

We can now calculate two different phase space functions: one that is the phase space function based on the molecular orbitals $f_m(\boldsymbol{r}, \boldsymbol{p})$, and one that is the sum of the phase space functions for the atomic orbitals $f_a(\boldsymbol{r}, \boldsymbol{p})$. We will then be able to see the changes in the phase space arising from the formation of the chemical bond.

If we write the wavefunction in coordinate representation for each of the three systems of interest: the Li atom, the H atom, and the LiH molecule as a single Slater-determinant, we can use the methods of [4, 5] in calculating the two phase space functions. The result is

$$\begin{aligned} f_a(\boldsymbol{r}, \boldsymbol{p}) &= 2 f_{\mathrm{Li},1s}(\boldsymbol{r}, \boldsymbol{p}) + f_{\mathrm{Li},2s}(\boldsymbol{r}, \boldsymbol{p}) + f_{\mathrm{H},1s}(\boldsymbol{r}, \boldsymbol{p}) \\ f_m(\boldsymbol{r}, \boldsymbol{p}) &= 2 f_{\mathrm{LiH},1\sigma}(\boldsymbol{r}, \boldsymbol{p}) + 2 f_{\mathrm{LiH},2\sigma}(\boldsymbol{r}, \boldsymbol{p}) \end{aligned} \tag{2}$$

where each of the phase space functions for the orbitals can be found by transforming the corresponding wavefunction in coordinate representation according to

$$f_i(\boldsymbol{r}, \boldsymbol{p}) = \frac{1}{\pi^3} \int \psi_i^*(\boldsymbol{r} - \boldsymbol{r}')\psi_i(\boldsymbol{r} + \boldsymbol{r}')\, e^{-2i\boldsymbol{p}\cdot\boldsymbol{r}'}\, d\boldsymbol{r}'. \tag{3}$$

The atomic wavefunctions are written as a linear combination of Gaussian s-functions taken from [10], and the molecular wavefunctions are found by performing a HF–SCF calculation [11] with the same total basis set extended with a Gaussian p_z-function placed on the Li nucleus.

All the obtained data, including the ones from Ref. [10] are collected in Table 1.

It is now a trivial although cumbersome matter of integrations to find the two phase space functions, $f_a(\boldsymbol{r}, \boldsymbol{p})$ and $f_m(\boldsymbol{r}, \boldsymbol{p})$, using Eqs. (2) and (3).

3. Results

Interpreting the phase space functions as electron densities it turns out that it is convenient to use cylindrical coordinates with the z-axis as the cylinder-axis for both $\boldsymbol{r}$ and $\boldsymbol{p}$:

$$\begin{aligned} (x, y, z) &= (r \cos \theta, r \sin \theta, z) \\ (p_x, p_y, p_z) &= (p_r \cos p_\theta, p_r \sin p_\theta, p_z) \end{aligned} \tag{4}$$

Table 1. Data for atomic and molecular orbitals

Type of	Orbital	Expansion Coefficients					
orbital	exponent	H, 1*s*	Li, 1*s*	Li, 2*s*	LiH, 1σ	LiH, 2σ	
Li, *s*	1359.4466	0	0.000844	0.000132	0.000843	−0.000097	[a]
	204.02647	0	0.006485	0.001017	0.006481	−0.000746	
	46.549541	0	0.032466	0.005124	0.032446	−0.003734	
	13.232544	0	0.117376	0.019108	0.117302	−0.013501	
	4.286148	0	0.294333	0.050977	0.294438	−0.034276	
	1.495542	0	0.450345	0.098292	0.449116	−0.076380	
	0.542238	0	0.255307	0.131809	0.256604	−0.067663	
	0.073968	0	0.008132	−0.573351	0.007291	0.241115	
	0.028095	0	−0.002444	−0.521225	−0.004027	0.021327	
Li, p_z	0.15	0	0	0	−0.005299	0.163795	
H, *s*	837.21974	0.000112	0	0	−0.000001	0.000083	[a]
	133.52431	0.000895	0	0	0.000009	0.000665	
	27.704222	0.004737	0	0	0.000047	0.003522	
	7.825986	0.019518	0	0	0.000193	0.014512	
	2.565036	0.065862	0	0	−0.000221	0.051396	
	0.938258	0.178008	0	0	0.002803	0.103057	
	0.372145	0.350387	0	0	0.000631	0.253072	
	0.155838	0.391529	0	0	0.000829	0.210113	
	0.066180	0.133721	0	0	0.002451	0.258367	

[a] Contracted during the molecular orbital calculations

The two phase space functions depend on the two angles θ and p_θ only through the difference $\theta - p_\theta$ which can be taken as a consequence of the rotational symmetry around the molecular axis of the electron density in coordinate space.

Integration over θ and p_θ leaves us with two functions of the type

$$f(r, z, p_r, p_z) \tag{5}$$

where

$$f(r, z, p_r, p_z) r\, dr\, dz\, p_r\, dp_r\, dp_z \tag{6}$$

describes the number of electrons in a small volume element in the four dimensional phase subspace

$$\begin{aligned} &r, p_r \in [0, \infty[\\ &z, p_z \in]-\infty, \infty[\end{aligned} \tag{7}$$

In order to depict the two phase space functions we have chosen to integrate over two of the four variables in Eqs. (5–7) and then make contour plots showing the dependence on the two remaining ones.

Thus Figs. 1, 3, and 5 show $f_a(z, p_z)$, $f_a(z, p_r) \cdot p_r$, and $f_a(r, p_r) \cdot r p_r$, and Figs. 2, 4, and 6 show the same dependences for f_m.

A comparison between Figs. 1 and 2 and between Figs. 3 and 4 gives us at once that the bond between the two atoms for a major part is formed by removing

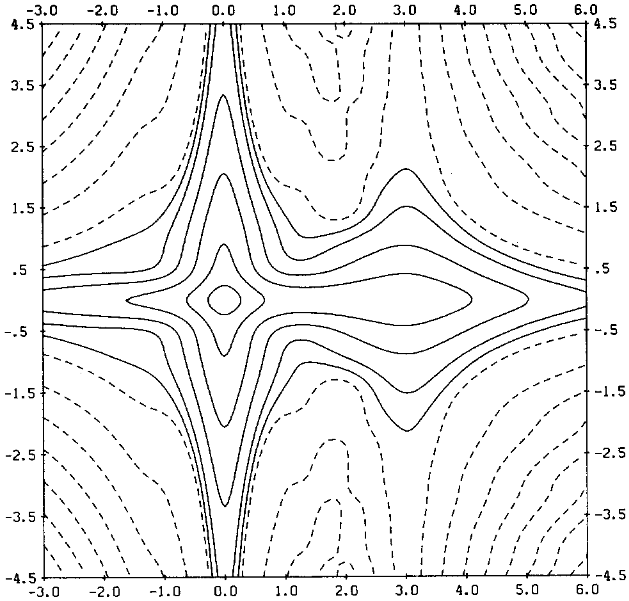

Fig. 1. Contour curves for the atomic phase space function $f_a(z, p_z)$ for LiH in a (z, p_z) phase plane. The Li nucleus is placed at $z = p_z = 0$, and the H nucleus at $z = 3.015$, $p_z = 0$. Contour values: ——: 0.8, 0.5, 0.25, 0.1, 0.03, 0.01: – – –; 0.0; ——: −0.01, −0.3

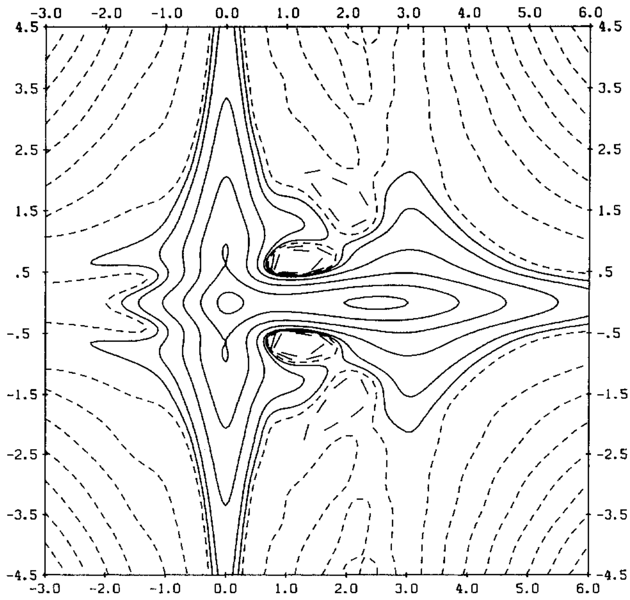

Fig. 2. Contour curves for the molecular phase space function $f_m(z, p_z)$ for LiH presented as $f_a(z, p_z)$ in Fig. 1

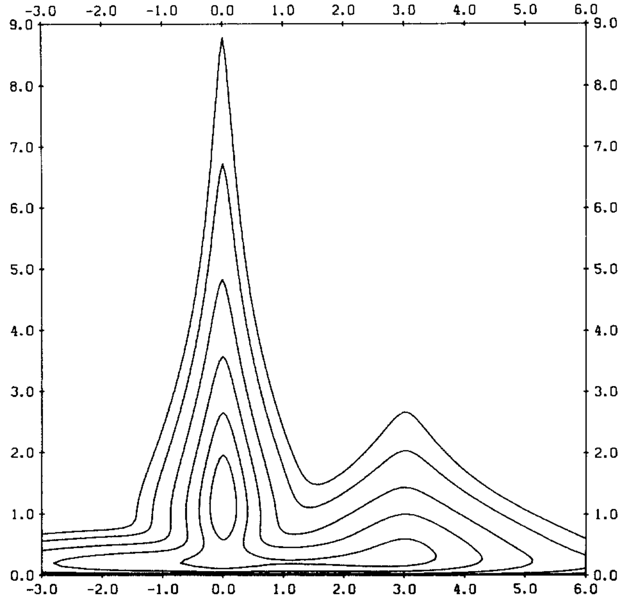

Fig. 3. Contour curves for the atomic phase space function $f_a(z, p_z) \cdot p_r$ for LiH in a (z, p_r) phase plane. The Li nucleus is placed at $z = p_r = 0$, and the H nucleus at $z = 3.015$, $p_r = 0$. Contour values: ——: 0.8, 0.5, 0.25, 0.1, 0.03, 0.01

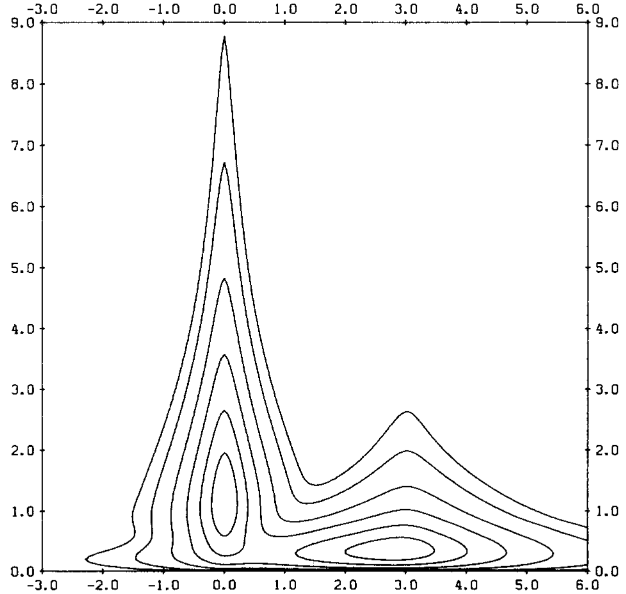

Fig. 4. Contour curves for the molecular phase space function $f_m(z, p_r) \cdot p_r$ for LiH presented as $f_a(z, p_r) \cdot p_r$ in Fig. 3

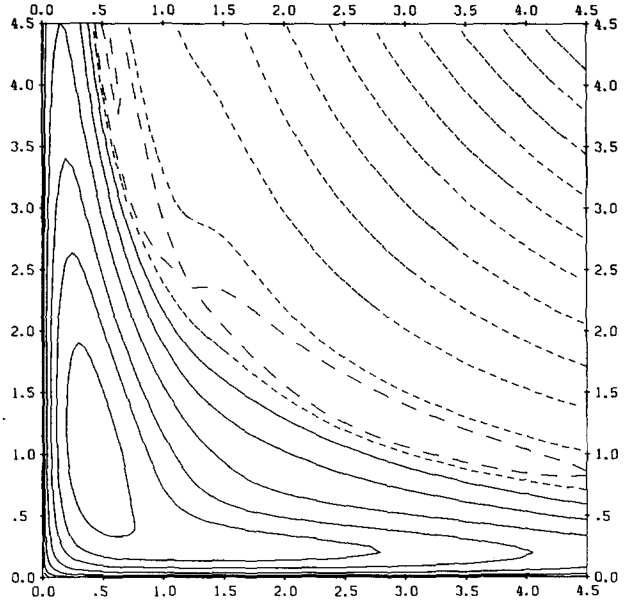

Fig. 5. Contour curves for the atomic phase space function $f_a(r, p_r) \cdot rp_r$ for LiH in a (r, p_r) phase plane. The two nuclei are placed at $r = p_r = 0$. Contour values: ——: 1.2, 0.8, 0.5, 0.25, 0.1, 0.03; ---: 0.0; —–—: −0.01, −0.03

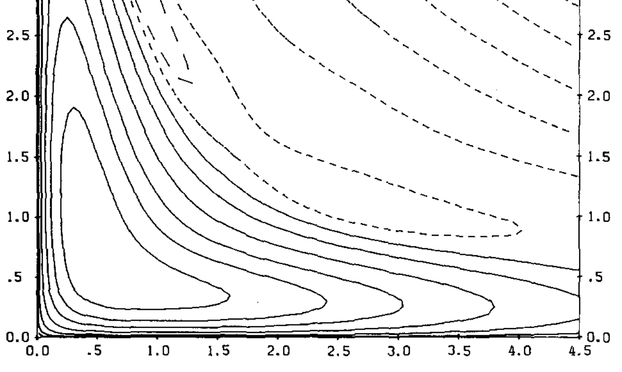

Fig. 6. Contour curves for the molecular phase space function $f_m(r, p_r) \cdot rp_r$ for LiH presented as $f_a(r, p_r) \cdot rp_r$ in Fig. 5

some of the electron densities from the region in coordinate space far behind the Li nucleus with small momenta to the region between the two nuclei still with small momenta.

However, some of the most significant changes occur in regions in phase space with $|p_z| \simeq 1$ near the Li nucleus as is seen in Figs. 1 and 2. The de Broglie wavelength corresponding to the momentum p is the well known

$$\lambda = 2\pi/p. \tag{8}$$

Thus, $|p_z| \simeq 1$ corresponds in the LiH moleucle to waves with wavelengths in the direction of the molecular bond of $\lambda \simeq 2R$. For many years it has been well known [12] that the most significant changes in momentum space under the formation of a bond occur for those wavelengths. Application of the phase space makes it possible to localise those changes to be centered around the Li nucleus in the LiH molecule.

C. A. Coulson [12] states that the formation of a bond will move the distribution for the component of the momentum in the bond direction towards smaller values, and move the distribution for the component perpendicular to the bond towards higher values. This fact can be confirmed to be true locally too as the Figs. 1–6 show.

In the analysis of the phase space function for atomic structures [3, 5] it was shown that for $|\boldsymbol{r}|$, $|\boldsymbol{p}| \gtrsim 2$ the phase space function oscillated around the value 0 with rapidly decreasing amplitude. In Figs. 1, 2, 5, and 6 we refind the oscillations far away from the nuclei. In fact, it turns out that they are almost for the sum of the atomic phase space functions and for the molecular phase space functions. Finally, it is remarkable that they do not show up in the Figs. 3 and 4.

4. Conclusion

We have seen how the formation of a bond changes the electron density in phase space when interpreting Wigner's phase space function as this density. It is realised that the formation of a bond is a very local phenomenon also in phase space, so that only little away from the bonding region it is difficult to distinguish between a diatomic molecule and the two non-interacting atoms.

We consider the most interesting figures in the present paper to be the Figs. 1 and 2, since we here observe the largest changes when the bond is created. It has been shown [16, 17] that when forming the bond between the Li and the H atoms the charge density in coordinate space decreases close to the Li nucleus between the two nuclei, and increases in a large neighbourhood of the H nucleus and close to the Li nucleus beyond the nucleus. Thus, analysing Figs. 1 and 2 we realise that in the LiH case those charge changes near the nucleus for the atom from which charge is removed, mainly happen for that part of the electron density in momentum space which corresponds to the de Broglie wavelength $\lambda = 2R$ in the bond direction.

This statement, obviously true for the LiH molecule, is interesting, since it gives a more comprehensive description of a bond than the usual one: considering coordinate and momentum space separately, we find properties that are refound locally when examining both spaces at the same time. But before this can be established as a global trend in the formation of chemical bonds it should be investigated what happens in other diatomic heteronuclear systems, in diatomic homonuclear systems, and in sytems like the benzene molecule.

Acknowledgement. The author would like to thank Professor Jens Peder Dahl for his continued interest and inspiration during the present work. Furthermore, the help of Dr. Helge Johansen in performing the SCF calculation is gratefully acknowledged.

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Received January 25, 1983