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Hole localization versus delocalization in symmetric molecular ions

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Hartree-Fock (HF) and local-density approximation (LDA) calculations of holes in symmetric molecular ions lead to conflicting results on the sign of the energy associated with reducing the symmetry. According to the HF theory, this energy can only be negative because it corresponds to a less restricted wave function. According to the LDA, it can only be positive because it is mostly electrostatic force that concentrates the hole charge in the vicinity of a single atom. In the present paper, we discuss these diverging views and present some LDA results for molecular ions with broken symmetry.

I. INTRODUCTION

In the calculation of the ionization potential (IP) of a symmetric molecule one must face the problem of assigning the symmetry to the molecular ion. Usually one assumes that the ion has the full symmetry of the parent molecule, but the possibility of it having a lower symmetry corresponding to a localized hole cannot be discarded. We are thinking of molecules such as Li_2, CO_2, N_2, etc., that is, molecules with equivalent atoms and a plane of symmetry. Rigorously speaking, if the nuclei are maintained at their symmetric positions, the exact solutions of the many-electron Schrödinger equation are always symmetric or, at least, irreducible representations of the group. For instance, for the $H_2{}^+$ ion, the lowest states are always even or odd with respect to the plane of symmetry, independent of the distance between the protons. A state in which the electron is attached to just one proton could not be exactly stationary because the electron would tunnel to the other proton, though with very low frequency if the disance is large. The asymmetric solution for which the electron is localized at one side only, though not exactly stationary, may be almost so (slow decay), and as such describe the state of the system in a real experiment. Indeed, it is most unlikely that a system of two protons, miles apart, and a single electron will ever be observed in a state where the electron is shared, half for each proton. It is a common expectation that the opposite is true and the electron will be found wholly at one side.

Under certain circumstances, self-consistent-field (SCF) methods such as Hartree-Fock (HF) and the local-density approximation (LDA), though approximate methods, are sophisticated enough to give these asymmetric ion solutions, aside from the symmetric solutions that always exist. In this sense a SCF calculation can do even better than an exact calculation that would yield only symmetric ions. On the other hand, SCF methods give no indication of the lifetime of these asymmetric ions, for the simple reason that they are treated as exactly stationary. In other words, when giving results for the asymmetric ion, the SCF methods cannot describe whether they are better or worse than the symmetric solution. Since the early work of Bagus and Schaefer[1] there have been a number of investigations concerning these asymmetric ions.[2-9] The studies were usually performed using HF or configuration-interaction (CI) techniques to describe the ionization of core electrons in molecules, that is, to calculate highly excited molecular ions. By removing the symmetry constraints in the Hartree-Fock solution, one increases the total relaxation energy, lowering the total energy of the molecular ion. In other words, common to all HF results is the fact that the asymmetric ion has a lower energy than the symmetric ion. This result is frequently understood with the argument that the removal of the symmetry constraints can only lead to a better minimum of the variational energy. Of course, when dealing with core ionization (highly excited molecular ions) it is not required that the energy should be a minimum, but only that it should be a stationary point, so the argument fails.

To those used to electronic-structure calculations based on the density-functional theory (DFT), or better, based on the local-density approximation, the HF result above is a complete surprise. For instance, take the case of a crystal. A symmetric hole would be described by a Bloch function that extends throughout the infinite crystal (delocalized), while an asymmetric hole would be localized at an atom and its immediate neighborhood (localized hole). Now, all LDA calculations give an ionization potential for the asymmetric ion (localized hole) larger than the IP for the Bloch-state hole.[10-12] In the case of molecules, the results of Connolly *et al.*,[7] obtained with the multiple-scattering method, also present this common feature of the LDA.

Thus the LDA is in clear opposite to HF when dealing with the spontaneous symmetry breaking of the ion. In Table I we show the extent of contradiction between the LDA and HF, by comparing the ionization potentials for symmetric and asymmetric core holes. Clearly, in the case of the LDA

TABLE I. Ionization potentials to the 1s-hole ions (in rydbergs).

	HF		LDA		
	Sym.	Asym.	Sym.	Asym.	Expt.
Li_2	4.761[a]	4.530[a]	4.387[b]	4.881[b]	4.86
N_2	30.891[c]	30.200[c]	29.430[b] 29.921[d]	30.797[b] 30.818[d]	30.13
O_2	40.908[e]	39.883[e]	39.325[b]	40.440[b]	40.0

[a] Reference 8.
[b] Present work.
[c] Reference 19.
[d] Reference 7.
[e] Reference 1.

$$V_{\mathrm{IP(asym)}} > V_{\mathrm{IP(sym)}} ,$$

while the opposite is true for HF, the inequalities for each method being consistently obtained by different authors. One must recall that, though not perfect, the LDA leads to a physical insight of the one-particle description through which one obtains a very good understanding of the electronic structure. Then, based on LDA arguments we can discuss hole localization versus delocalization in the following terms.

(i) Suppose a symmetric core hole (delocalized) is formed. Since its wave function is finite only near the nuclei, where the electronic charge density is large, exchange-correlation effects are relatively unimportant. Now, to concentrate the hole density at only one atom one must make the *positive* electrostatic force work. Therefore, the IP for the asymmetric ion should be larger by the amount of work, and the symmetric ion should have lower energy.

(ii) Suppose a valence symmetric hole (delocalized) is formed. Now the wave function is large in the interatomic regions, where the electronic charge density may not be large at all. Then it is difficult to guess the relative importance of the electrostatic energy and exchange-correlation energy. Only an actual calculation will decide the dominating energy. For those molecules with few valence electrons one might have an exchange-correlation-dominated situation where the symmetric ion (delocalized hole) would have a higher energy than the asymmetric ion (localized hole). In this case, the ground state of the ion (a hole in the highest valence state) would be asymmetric, corresponding to the common expectation that the removal of the symmetry constraints could only lower the energy. But observe that this expectation can only refer to the ionic ground state, and it can only result from the exchange-correlation energy.

The purpose of this paper is twofold. On the one hand, we want to call the reader's attention to the contradiction between the LDA and HF. On the other hand we want to present some LDA results for molecules with varying degrees of exchange-correlation domination. In Sec. II, we discuss in a formal way what to expect from the LDA on the problem of spontaneous symmetry breaking. In Sec. III we review our LDA method, the variational cellular method, which avoids the muffin-tin potential format, but still has some limitations. In Sec. IV we present our results and in Sec. V we present conclusions.

II. SYMMETRY BREAKING IN THE LDA

The ionization potential of a molecule is defined as the difference

$$V_{\mathrm{IP}} = E(-1) - E(0) \tag{1}$$

between the energies of the molecular ion $E(-1)$ and that of the neutral molecule $E(0)$. Here, the argument (-1) means that one electron has been removed from a certain one-electron state α. Within the LDA it is possible to define the total energy even for noninteger occupation numbers f_α (Slater's transition-state method)[13] and even prove that the derivative of the total energy with respect to the occupation is the one-particle eigenvalue[14]

$$\frac{\partial E}{\partial f_\alpha} = \varepsilon_\alpha . \tag{2}$$

The eigenvalue ε_α is itself a function of the occupations f_α, but, as verified by many authors,[15] it is a mostly linear function, so that the derivative

$$\frac{\partial \varepsilon_\alpha}{\partial f_\alpha} = 2S_\alpha \tag{3}$$

is practically independent of the occupation.

For reasons that will shortly become clear, we will refer to the derivative S_α in Eq. (3) as the "self-energy." Recalling that, within the LDA, the Schrödinger equation potential is

$$V(r) = V_{\mathrm{ext}}(\mathbf{r}) + 2\int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\partial E_{\mathrm{xc}}}{\partial \rho(\mathbf{r})} \tag{4}$$

(rydberg units are being used), where E_{xc} is the exchange-correlation functional, and where the total number density is

$$\rho(\mathbf{r}) = \sum_\alpha f_\alpha \rho_\alpha(\mathbf{r}) \tag{5}$$

with

$$\rho_\alpha(\mathbf{r}) = [\psi_\alpha(\mathbf{r})]^\dagger \psi_\alpha(\mathbf{r}) , \tag{6}$$

where $\psi_\alpha(\mathbf{r})$ is the one-particle wave function for the state α, then one obtains the self-energy from simple first-order perturbation theory,

$$S_\alpha = \int\int d\mathbf{r}\,d\mathbf{r}'\rho_\alpha(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\rho_\alpha(\mathbf{r}') + \tfrac{1}{2}\int\int d\mathbf{r}\,d\mathbf{r}'\rho_\alpha(\mathbf{r})\frac{\delta^2 E_{\rm xc}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\rho_\alpha(\mathbf{r}') \ . \tag{7}$$

Furthermore, if S_α does not depend on the occupation f_α,

$$\varepsilon_\alpha(f_\alpha) = \varepsilon_\alpha(0) + 2f_\alpha S_\alpha \ , \tag{8}$$

and integrating Eq. (2),

$$E(f_\alpha) = E(0) + \varepsilon_\alpha(0)f_\alpha + S_\alpha f_\alpha^2 \ , \tag{9}$$

so that

$$V_{\rm IP} = -\varepsilon_\alpha(0) + S_\alpha = -\varepsilon_\alpha(-\tfrac{1}{2}) \ . \tag{10}$$

which is the transition-state result.

Equation (10) gives the ionization potential as an algebraic sum of two terms: (i) the eigenvalue $\varepsilon_\alpha(0)$ for the neutral molecule of course does not depend on whether the ion is symmetric or asymmetric; (ii) the self-energy S_α, whose expression is given by Eq. (7), may depend much on the degree of asymmetry of the ion. Indeed, consider the first term in Eq. (7), which is the electrostatic energy term. First of all, this term is clearly a self-energy term, giving the name for the symbol S_α. Second, this term is positive definite, making the IP larger than the negative of the eigenvalue of the neutral molecule. Third, if the hole number density $\rho(\mathbf{r})$ is distributed between equivalent atoms, the term is greatly reduced. For instance, in the extreme limit when $\rho_\alpha(\mathbf{r})$ is the Bloch-state number density of a hole in an infinite crystal, the self-energy S_α is exactly zero, in which case the IP follows Koopmans's theorem. Therefore, if the exchange-correlation term of the self-energy can be neglected, that being the case of core holes whose wave functions are non-negligible only in the regions of high electronic density, the process of delocalizing the hole lowers the ionization potential, as discussed in the Introduction.

To fully understand the behavior of the self-energy under localization or delocalization of the hole, we must also study the second term of Eq. (7). Though we have not used the $X\alpha$ exchange correlation, but an expression due to Gunnarsson and Lundqvist,[16] we follow the present discussion by assuming

$$E_{\rm xc}[\rho] = -\alpha\int d\mathbf{r}\,\rho(\mathbf{r})^{4/3} \ . \tag{11}$$

The functional derivatives are

$$\frac{\delta E_{\rm xc}}{\delta\rho(\mathbf{r})} = -\tfrac{4}{3}\alpha\rho(\mathbf{r})^{1/3} = -\tfrac{4}{3}\alpha\int d\mathbf{r}'\rho(\mathbf{r}')^{1/3}\delta(\mathbf{r}'-\mathbf{r}) \ , \tag{12}$$

$$\frac{\delta^2 E_{\rm xc}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} = -\tfrac{4}{9}\alpha\frac{\delta(\mathbf{r}-\mathbf{r}')}{\rho(\mathbf{r})^{2/3}} \ . \tag{13}$$

Then the second term of the self-energy becomes

$$\tfrac{1}{2}\int\int d\mathbf{r}\,d\mathbf{r}'\rho_\alpha(\mathbf{r})\frac{\delta^2 E_{\rm xc}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\rho_\alpha(r) = -\tfrac{2}{9}\alpha\int d\mathbf{r}\frac{\rho_\alpha(\mathbf{r})\rho_\alpha(\mathbf{r})}{\rho(\mathbf{r})^{2/3}} \ , \tag{14}$$

which is negative definite, and which is important only when the hole density $\rho_\alpha(\mathbf{r})$ is large where the total electronic density $\rho(\mathbf{r})$ (denominator) is small. For valence electron, especially in molecules where they are not many, the second term of the self-energy might even dominate the positive-definite first term. Then the net self-energy would be negative and larger in absolute value for the localized hole than for the delocalized one. Only in this circumstance would the asymmetric ground state of the ion have a lower energy than the symmetric ion; that is, relaxing the symmetry constraints would lead to a lower energy. Again we reach the conclusions advanced in the Introduction.

III. REVIEW OF THE VARIATIONAL CELLULAR METHOD

Our LDA results were calculated with the variational cellular method (VCM), in its latest version.[17] This method, with marked advantages over the classical multiple-scattering method.[18] both in precision and speed, begins by partitioning the space into cells. A point $\mathbf{r}$ belongs to cell i if

$$\gamma_i(\mathbf{r}-\mathbf{a}_i)^2 - \gamma_1 R_i^2 < \gamma_j(\mathbf{r}-\mathbf{a}_j)^2 - \gamma_j R_j^2 \tag{15}$$

for all other cells j. Here $\mathbf{a}_i$ and $\mathbf{a}_j$ are the cell centers (the nuclei), and γ and R are cell parameters. If $\gamma_i = \gamma_j$, the cell boundary between cells i and j is a plane, which follows readily from Eq. (15) if the equality is used instead of the inequality. This choice of γ is normally used. The parameter R controls the size of the cell, so that usually we choose it equal, or proportional, to the covalent radius. Aside from the atomic cells centered at the nuclei, one also defines an outer cell enveloping the molecule. For this outer cell 0, the center $\mathbf{a}_0$ is chosen so that the molecular symmetry is preserved; γ_0 (which must be negative) and R_0 are chosen so that the atomic cells are not much extended.

In the cell-divided space we expand the one-electron wave functions $\psi_\alpha(\mathbf{r})$ and the Coulomb potential $c(\mathbf{r})$ in spherical harmonics. Aside from these functions, one also defines the following.

(i) The model number density

$$n(r) = [\rho(\mathbf{r})]_{\rm sph.\ av.} \ , \tag{16}$$

that is, the spherical average within each cell of the true number density of Eq. (5).

(ii) The potential intervening into the one-particle Schrödinger equation

$$V(r) = \left[c(\mathbf{r}) + \frac{\delta E_{\rm xc}}{\delta\rho(\mathbf{r})}\right]_{\rm sph.\ av.} \ , \tag{17}$$

which is also spherical within each cell.

The total molecular (or ionic) energy is a functional of the four functions $\psi_\alpha(\mathbf{r})$, $c(\mathbf{r})$, $n(r)$ and $V(r)$

$$E[\psi_\alpha,c,n,V]=\sum_\alpha f_\alpha \varepsilon[\psi_\alpha,V]-\int d\mathbf{r}\, V(r)n(r)+U[n-p,c]-S[p]+E_{\text{xc}}[n]\ , \quad (18)$$

where $\varepsilon[\ ]$ is the one-particle energy functional, $U[\ ]$ is the electrostatic energy functional, p is the proton number density (a collection of δ functions), and $S[\ ]$ is the proton self-energy. The power of the VCM lies in that the total energy is stationary for arbitrary variations in the four functions if (i) the one-electron wave functions satisfy the Schrödinger equation, (ii) the Coulomb potential satisfies the Poisson equation, (iii) the model number density $n(r)$ equals the true number density $\rho(\mathbf{r})$, and (iv) the Schrödinger potential V equals that of Eq. (4), which is that of Eq. (17) without the spherical averaging. Thus small deviations from any of the four variational conditions produce only a second-order error in the total energy. Compared to the multiple-scattering method, the VCM avoids the constant-potential region that is usually unable to hold the valence charge in the neighborhood of the atoms, which it scatters through the whole molecule. For the study of localized hole states, we thought that this advantage could be very important.

The VCM is a self-consistent method where one starts from an approximate Schrödinger potential $V(r)$, obtains the wave functions $\psi_\alpha(\mathbf{r})$ and eigenvalues, calculate the model number density $n(r)$ and the Schrödinger potential $V(r)$, and repeats the iterations till self-consistency is achieved. Of course the result depends on the assumed occupation numbers f_α. Instead of calculating the IP through its definition [Eq. (1)], it is certainly faster to use the transition-state result [Eq. (10)], which identifies the IP with the negative of the eigenvalue at a depletion of half electron. Since the number density of a molecule is the functional derivative of the energy with respect to an external potential,

$$\rho(\mathbf{r})=\frac{\delta E}{\delta v_{\text{ext}}(\mathbf{r})}\ , \quad (19)$$

from Eqs. (1) and (10) we readily conclude that the hole number density is exactly the same as the number density for the state α being half-depleted

$$\frac{\delta\varepsilon_\alpha(-\frac{1}{2})}{\delta v_{\text{ext}}(\mathbf{r})}=\psi_\alpha(\mathbf{r})^*\psi_\alpha(\mathbf{r})\ , \quad (20)$$

the wave functions of the other states giving no contribution to the hole number density. A plot of Eq. (20) will show how much the hole is localized in an atom.

We found that a symmetric ion solution always existed within the VCM. For the core-ionized ions, we were always able to find an asymmetric solution (localized hole). In the case of valence electrons, it was frequently difficult to make the VCM equations to converge to an asymmetric ion solution. To do so, we started from the converged potential for the symmetric ion, introduced an artificial asymmetrizer (usually by making the basis sets of functions different for the equivalent atoms), let the VCM program run for some iterations, then removed the asymmetrizer and let the VCM program run freely till self-consistency was achieved. In the case of valence electrons, self-consistency frequently restored the symmetric condition. Thus we are convinced that an asymmetric valence ion is not always a stationary solution of the LDA equations, at least in their VCM version. When both solutions exist, the symmetric and the asymmetric, there should be two IP's, at least a broadband. The transition to one of the ions, either symmetric or asymmetric, could dominate the other transition, depending on the relative cross sections. But this latter point is far outside the scope of the present work.

IV. RESULTS AND DISCUSSION

We calculated three dimmers and two simple polyatomic molecules. The VCM parameters for the calculations are reported in Table II. The calculations were performed at the experimental geometry of the neutral ground-state molecules. The molecules that were studied have the common feature of having a mirror plane that is removed from the symmetry group of the ion when the hole becomes localized at one side.

We used the transition-state concept to determine the ionization potential. The symmetric ion with a hole density equally distributed between the two sides of the mirror plane could always be found. On the other hand, the asymmetric ion with its localized hole could be found only exceptionally. To reach the asymmetric solution, we ran some iterations where the bases for the expansion of the wave functions were different at the two sides of the mirror plane (asymmetrizer). Once the two sides were unbalanced, the asymmetrizer was removed; that is, the bases were made equal at the two sides, and the iterations were run till self-consistency was achieved. In most cases of the valence holes, self-consistency restored the full symmetry of the hole density, indicating that an asymmetric hole solution does not exist.

The results are presented in Tables III–VII. Discussion about these results naturally separates into core-hole ions and valence-hole ions. In the case of core holes, we could always find the asymmetric ion solution, together with the symmetric one. That means there are two ionization potentials for core-hole ions (within the LDA), one corresponding to the localized hole, the other corresponding to the delocalized one. In all cases, the ion with a localized hole has a larger IP than the ion with the symmetric hole, which is in opposition to the results obtained with HF (Ref. 1) (Table I), but in agreement with our argument requiring an extra electrostatic force to create the hole cloud at just one side of the molecule. Indeed, one observes from the tables a sharp increase in the self-energy of the core holes when going from delocalized to localized at one side. Roughly, the self-energy of the core hole is multiplied by a factor of 2 when it is localized [first term of Eq. (7)]. It is also interesting to observe that the self-energies of C(1s) in CO_2 and C_2H_4 (asym.) are nearly equal, indicating that one is dealing with a mostly atomic, and not molecular, state. The same situation happens for the self-energy of O(1s) in O_2 and CO_2.

TABLE II. Cell parameters.

	Diatomic molecules		
	Li_2	N_2	O_2
$d_{X\text{-}X}$ (a.u.) interatomic distance	5.051	2.068	2.282
R_i (a.u.)	3.5	2.0	1.8
R_0 (a.u.)	6.0	3.0	3.0
γ_i	1.0	1.0	1.0
γ_0	-2.0	-1.8	-1.0
Full symmetry group	$D_{\infty h}$	$D_{\infty h}$	$D_{\infty h}$
Broken symmetry group	$C_{\infty v}$	$C_{\infty v}$	$C_{\infty v}$

	Polyatomic molecules	
	CO_2	C_2H_4
C-C interatomic distance (a.u.)		2.5303
C-X interatomic distance (a.u.)	2.20	2.0526
R_C (a.u.)	1.10	2.20
R_X (a.u.)	1.10	1.49
R_0 (a.u.)	3.30	4.00
γ_C	1.0	1.0
γ_X	1.0	2.0
γ_0	-1.0	-0.6
Full symmetry group	$D_{\infty h}$	D_{2h}
Broken symmetry group	$C_{\infty v}$	C_{2v}

TABLE III. Results for Li_2 (in rydbergs).

	$D_{\infty h}$					$C_{\infty v}$	
Symmetry level	Ionization potential Expt.[a]	VCM (sym.)	Eigenvalue	Self-energy	Symmetry level	IP VCM (asym.)	Self-energy
$2\sigma_g$	0.40	0.4354	-0.2570	0.1784	2σ	0.4164	0.1594
$1\sigma_u$	4.73	4.3865	-3.7283	0.6582	1σ	4.8813	1.1530
$1\sigma_g$	4.86	4.3871	-3.7303	0.6568	1σ	4.8813	1.1510

[a] Reference 20.

TABLE IV. Results for N_2 (in rydbergs).

	$D_{\infty h}$					$C_{\infty v}$	
Symmetry level	Ionization potential Expt.[a]	VCM (sym.)	Eigenvalue	Self-energy	Symmetry level	IP VCM (asym.)	Self-energy
$3\sigma_g$	1.14	1.1920	-0.7716	0.4204	4σ	1.4601	0.6885
π_u	1.23	1.2199	-0.8134	0.4065	π	0.9167	0.1033
$2\sigma_u$	1.37	1.3964	-0.9975	0.3989	3σ	1.6349	0.6374
$2\sigma_g$	2.74	2.2153	-1.7729	0.4424	2σ	2.5068	0.7339
N(1s)	30.13	29.4297	-27.9303	1.4994	N(1s)	30.7968	2.8665

[a] Reference 21.

TABLE V. Results for O_2 (in rydbergs).

	$D_{\infty h}$					$C_{\infty v}$	
Symmetry level	Ionization potential Expt.[a]	VCM (sym.)	Eigenvalue	Self-energy	Symmetry level	IP VCM (asym.)	Self-energy
π_g	0.96	0.6625	-0.2726	0.3899	2π		
π_u	1.31	1.4220	-1.0282	0.3938	1π		
$3\sigma_g$	1.55	1.4723	-1.0832	0.3891	4σ		
$2\sigma_u$	2.05	1.9836	-1.5890	0.3945	3σ		
$2\sigma_g$	3.06	2.6681	-2.2473	0.4208	2σ		
O(1s)	40.0	39.3254	-37.7410	1.5844	O(1s)	40.4406	2.6996

[a] Reference 21.

TABLE VI. Results for CO_2 (in rydbergs).

Symmetry level	$D_{\infty h}$ Ionization potential		Eigenvalue	Self-energy	Symmetry level	$C_{\infty v}$ IP	Self-energy
	Expt.[a]	VCM (sym.)				VCM (asym.)	
π_g	1.01	1.0575	−0.7135	0.3440	2π		
π_u	1.29	1.3757	−1.0254	0.3503	1π		
$3\sigma_u$	1.33	1.2356	−0.8905	0.3451	6σ		
$4\sigma_g$	1.43	1.3359	−0.9945	0.3414	5σ		
$2\sigma_u$	2.73	2.4325	−2.0654	0.3671	4σ		
$3\sigma_g$	2.73	2.4696	−2.1126	0.3570	3σ	2.4982	0.3856
C(1s)	21.86	22.0287	−19.8059	2.2228	C(1s)		
O(1s)	39.75	39.1662	−37.6406	1.5256	O(1s)	40.2891	2.6485

[a] Reference 22.

TABLE VII. Results for C_2H_4 (in rydbergs).

Symmetry level	D_{2h} Ionization potential		Eigenvalue	Self-energy	Symmetry level	C_{2v} IP	Self-energy
	Expt.[a]	VCM (sym.)				VCM (asym.)	
b_{3u}	0.77	0.8130	−0.5342	0.2788	$1b_1$		
b_{3g}	0.91	1.0361	−0.7468	0.2893	$2b_2$		
$3a_{1g}$	1.09	0.8355	−0.5560	0.2795	$4a_1$		
b_{2u}	1.15	1.2781	−0.9886	0.2895	$1b_2$		
$2b_{1u}$	1.39	1.5155	−1.2133	0.3022	$3a_1$		
$2a_{1g}$	1.73	1.8911	−1.5726	0.3185	$2a_1$		
C(1s)		21.1213	−19.9670	1.1543	C(1s)	21.9847	2.0177

[a] Reference 23.

In the case of valence holes, we obtained localized hole solutions for Li_2, N_2, and for the lowest valence state of CO_2. In the other cases, an asymmetric ion solution simply does not exist; that is, after the removal of the asymmetrizer, the self-consistent iterations restored the symmetric ion. The valence state of Li_2 is so shallow that we were unable to obtain a fully variational VCM solution for the neutral molecule, while it is very easy to converge the solution when the muffin-tin approximation is made. Without going that far, we chose to restrict the degrees of freedom of the VCM potential in the intersphere region, as described in Ref. 17, to reach convergence. The solution presents a clear case of exchange-correlation energy dominating over the Coulomb self-energy. When the hole could is localized at one side, the ion energy decreases, not increases. Thus the ground state of the Li_2^+

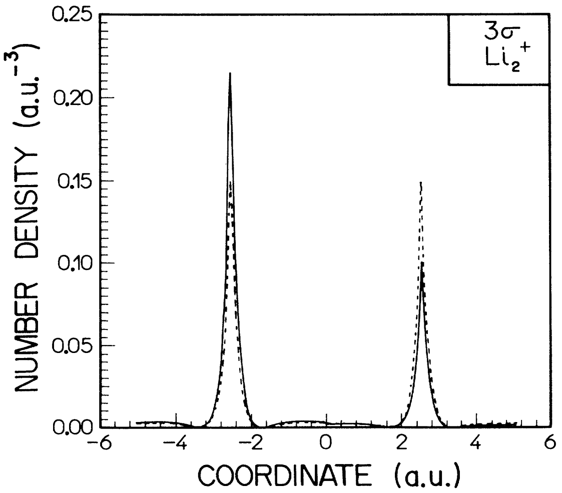

FIG. 1. Number density for the asymmetric 3σ valence hole for Li_2^+ along the molecular axis, compared to the number density for the symmetric hole ($2\sigma_g$).

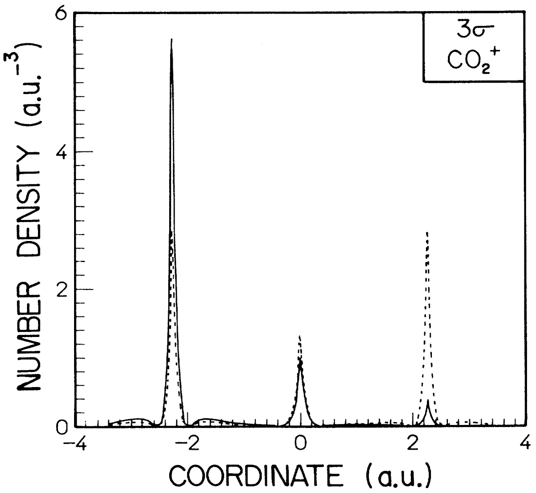

FIG. 2. Number density for the asymmetric 3σ valence hole of CO_2^+ along the molecular axis, compared to the number density for the symmetric hole ($3\sigma_g$).

ion becomes asymmetric. In Fig. 1 we compare the number densities of the symmetric and asymmetric 3σ valence holes of Li_2.

In the case of N_2, though the asymmetric solutions could be found, they compare poorly with the experimental results (IP), so that one may wonder whether these solutions are not an artifact of the LDA or VCM. Due to the hole localization, the smallest IP becomes that of the π hole, not that of the 4σ hole. This result could be expected becase the π hole is denser where the total electronic density is smaller, which increases the negative contribution of exchange-correlation energy to the self-energy.

The only localized valence hole of CO_2 is 3σ. This is mostly a O(2s) atomic state, with great energy, and can be almost classified as core. Thus one expects a Coulomb term to dominate the self-energy equation. For this reason, the IP to the localized-hole ion is larger. In Fig. 2 we compare the number densities for the symmetric and asymmetric holes.

V. CONCLUSIONS

Our results are in agreement with the physical intuition of the LDA: the ionization potentials of asymmetric core-hole ions are all larger than those of symmetric ions, while for valence holes, when the asymmetric ion exists, its IP will be larger or smaller depending on the degree of self-energy dominance by exchange correlation. On the other hand, the HF calculations of asymmetric core holes all lead to opposite results.

That the LDA and HF can lead to such contradictory results is perplexing; we think that the HF calculations of highly excited ionic states might be suffering from a defective orthogonalization to lower excited and ground ionic states. This possibility was suggested by Agren, Bagus, and Roos,[6] who showed that, with a limited configuration interaction, one could lower the core-hole IP of O_2 by almost 1 Ry. On the other hand, since the results of the LDA confirm our physical intuition, this method is very attractive.

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