

Tuning electronic eigenvalues of benzene via doping

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Using variable atomic numbers within molecular grand-canonical ensemble theory, the highest occupied Kohn-Sham eigenvalue of isoelectronic benzene derivatives is tuned. The performed transmutational changes correspond to the iterative doping with boron and nitrogen. The molecular Fukui function proves to be a reliable index in order to predict the changes in the highest occupied molecular orbital eigenvalue due to doping. © 2007 American Institute of Physics.

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I. INTRODUCTION

The design of molecular materials plays a crucial role in the growing field of molecular electronics.^{1,2} The elucidation and subsequent tuning of electronic structure and morphological details, which determine the charge mobilities, are crucial steps in the engineering of organic conducting films.³⁻⁵ The fundamental problem of engineering molecular properties through compositional variations, however, originates in the factorial scaling of the cardinal number of the high-dimensional space spanned by all possible stoichiometries and isomers.^{6,7} A successful compound design approach should enable an efficient and reliable *a priori* identification of promising compounds for material synthesis. Rational *in silico* approaches to materials design are rather recent⁸⁻¹³ and have not yet been used for the optimization of molecular properties relevant to this field.

Apart from the important aspects of synthesizability, stability, and material morphology,¹⁴ means to control electronic orbitals, especially highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital, via chemical doping are highly desirable to improve charge transport properties.² The idea of replacing CC units in organic compounds by BN pairs is of special interest since the electronic characteristics of polycyclic aromatic hydrocarbons could be altered significantly while maintaining crucial structural features.¹⁵ Boron nitride exemplifies this by being similar to graphite in many physical properties, e.g., having a graphitelike layer structure of alternating B and N. In analogy to the conversion of graphite to diamond, the layer structure of BN can even be converted into a tetrahedral diamond-like structure, known as boraxon.¹⁶ BN-doped benzene derivatives are another example of such systems. They have already been studied theoretically from the point of view of stability and electronic structure. Some of them were synthesized and characterized, e.g., borazine, or “inorganic benzene,” $B_3N_3H_6$, which has formal structural resemblance to benzene and very similar physical properties.¹⁷ The chemical

properties of borazine, however, indicate the absence of aromaticity and it has been suggested that properties of benzene and borazine can be interpolated through “hybrid” structures containing [HNBH] and [HCCH] moieties.¹⁸ Indeed, while 1,3-azaborine, BC_4NH_6 , exhibits significant bond delocalization, the 1,2- and 1,4-isomers appear to be best described as heterocyclic dienes.¹⁹ Similar calculations have been done for diazadiborines, $B_2C_2N_2H_6$, containing one [HCCH] and two [HNBH] moieties.¹⁸

In this study, we apply the recently introduced molecular grand-canonical ensemble density functional theory^{7,10,13} (DFT) to the problem of predicting the changes in HOMO eigenvalues of benzene derivatives due to doping at various sites in the molecule *without* the actual evaluation of the electronic structure of the corresponding mutants. If the predictions are sufficiently accurate, more efficient compound design algorithms for the tailoring of the electronic structure of more realistic molecules, such as hexabenzocoronene or pentacene, through compositional BN mutations become conceivable. In order to obtain these predictions, we compute the molecular Fukui function, i.e., the changes in the electrostatic potential due to a small variation in the HOMO occupation number. Based on this quantity, susceptibilities of the HOMO eigenvalue due to doping are obtained for all the respective nuclear sites. Iterating this procedure, we visit all mutants, analyze their electronic structure, and validate the accuracy by comparison to the corresponding eigenvalues.

Our choice of isolated benzene as a test system is motivated by the fact that (i) the number of all the possible benzene-derived mutants is small, allowing for a direct assessment of the HOMO values for all possible mutants and thorough control of all approximations; (ii) benzene can serve as a prototype for triphenylene and even larger polycyclic aromatic hydrocarbons, i.e., an extension of the proposed approach to these systems is rather straightforward.

The paper is organized as follows. Section II outlines the notion of a chemical space, summarizes the molecular grand-

canonical DFT framework, and provides the computational details. The ability of the grand-canonical approach to predict correct electronic structure is then addressed in Sec. III, which also summarizes the main results.

II. THEORY

A. Chemical space

All molecules consist of superimposed positive (nuclear) and negative (electrons) charge densities which have to integrate to the total number of protons, N_p , and electrons, N_e , of the system. The molecular charge is then the difference of these two numbers, $Q=N_p-N_e$.

We will restrict ourselves to *isoelectronic* benzene derivatives with $N_e=30$ valence electrons, i.e., N_e is constant and doped mutants are exclusively obtained from transmutational variations which result in the atomic numbers of B, C, and N. For this study, the chemical space is spanned by all the isoelectronic B- and N-doped benzene derivatives $B_{n'}C_{6-n'-n''}N_{n''}H_6$, where non-negative integer numbers n' and n'' can take the values 0, 1, 2, and 3. In total, there are 18 different neutral ($Q=0$) compounds which can be further divided into four stoichiometrical cases: one isomer for $n'=0$, three isomers for $n'=1$, eleven isomers for $n'=2$, and three isomers for $n'=3$. We allow also for charged compounds, where N_p is restrained to $30\pm\Delta N_p$ at the sites $\{R_I\}$ of the six nuclei $I=1, \dots, 6$ of benzene. For example, $Q=-1$ if one proton has been removed, i.e., one of the system's atoms decreased its atomic number (for example, changing carbon, $Z=6$, into boron, $Z=5$), and $Q=+1$ if a proton has been added, i.e., the system has been doped at one of the nuclear sites with an atomic number which was larger than before (for example, changing carbon, $Z=6$, into nitrogen, $Z=7$). Here, we only consider the charged mutants with $n'=n''\pm 1$ because in chemical space they represent intermediates between the neutral mutants ($n'=n''$). All the neutral and singly doped intermediates are depicted in Fig. 1.

B. Electronic structure and the molecular Fukui function

We first summarize the molecular grand-canonical ensemble DFT approach, and show how to apply it to the problem of tuning the HOMO eigenvalue. For more details and discussions of the theory the reader is referred to Refs. 7, 10, and 13.

Following Ref. 7, let us assume that molecules are represented by single particle electron and proton densities, $\rho(\mathbf{r})$ and $Z(\mathbf{r})$, which can be formally defined within the Born-Oppenheimer approximation. Furthermore, we assume the standard molecular Hamiltonian,

$$\hat{\mathcal{H}}_{\text{total}} = \hat{\mathcal{H}}_{ee} + \hat{\mathcal{H}}_{eZ} + \hat{\mathcal{H}}_{ZZ}, \quad (1)$$

where $\hat{\mathcal{H}}_{ee}$ and $\hat{\mathcal{H}}_{ZZ}$ are the Hamiltonians of the isolated electronic and nuclear subsystems and $\hat{\mathcal{H}}_{eZ}$ is the interaction between them, the total Kohn-Sham (KS) energy,^{28,29} $E[N_e, Z(\mathbf{r})]$, in terms of electron and proton densities is given by

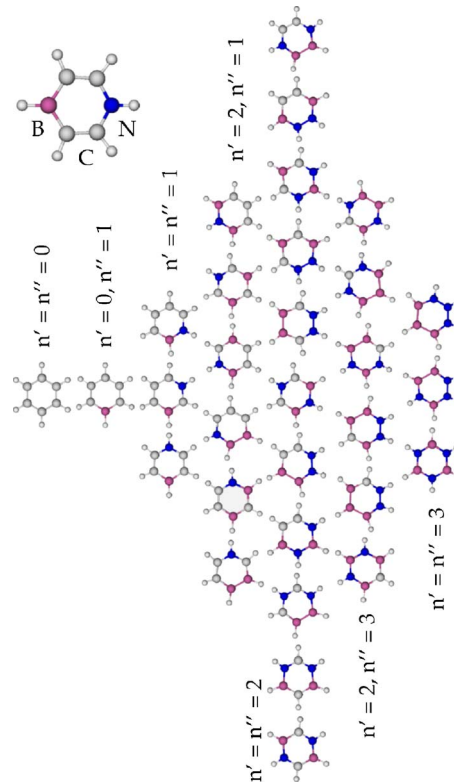


FIG. 1. Geometry optimized structures of all doped benzene derivatives and all anionic (singly charged) B-doped intermediates. The inset shows the color coding. Corresponding *cationic* intermediates can be obtained by exchanging B with N and n' with n'' .

$$\begin{aligned} E[N_e, Z] &= F_{ee}[\rho] + E_{eZ}[\rho, Z] + E_{ZZ}[Z] \\ &= F_{ee}[\rho] - \int d\mathbf{r} \rho(\mathbf{r}) v(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} Z(\mathbf{r}) \bar{v}(\mathbf{r}). \end{aligned} \quad (2)$$

Here, F_{ee} is the universal Hohenberg-Kohn functional, expressible within KS-DFT in terms of the noninteracting kinetic ($T_s[\{\phi_i\}]$, where $\phi_i(\mathbf{r})$ is a KS orbital), Hartree (E_H), and exchange-correlation (E_{xc}) energies,

$$F_{ee}[\rho] = T_{ee}[\rho] + V_{ee}[\rho] = T_s[\{\phi_i\}] + E_H[\rho] + E_{xc}[\rho]. \quad (3)$$

When considering a somewhat artificial “quantum-chemical” proton density, one has to take into account that protons defining the same nucleus would repel each other. This problem can be circumvented using a modified external potential of the form

$$\bar{v}(\mathbf{r}) = \int d\mathbf{r}' \frac{Z(\mathbf{r}') \text{erf}[\sigma|\mathbf{r}-\mathbf{r}'|]}{|\mathbf{r}-\mathbf{r}'|}, \quad (4)$$

for the nuclear Coulomb repulsion term. Here, the parameter σ can be chosen large enough that only a vanishingly small neighborhood around $|\mathbf{r}-\mathbf{r}'| \approx 0$ is excluded.

Derivatives of Eq. (2) with respect to the particle densities define the electronic and the nuclear chemical potentials, $\mu_e = \partial_{N_e} E$ and $\mu_n(\mathbf{r}) = \delta_{Z(\mathbf{r})} E$, respectively. μ_e has been related to the negative of the molecular electronegativity.^{20,21} Using Janak's theorem,²² which equates the partial derivative of the total potential energy with respect to the occupation number of a given KS orbital to the corresponding eigenvalue,

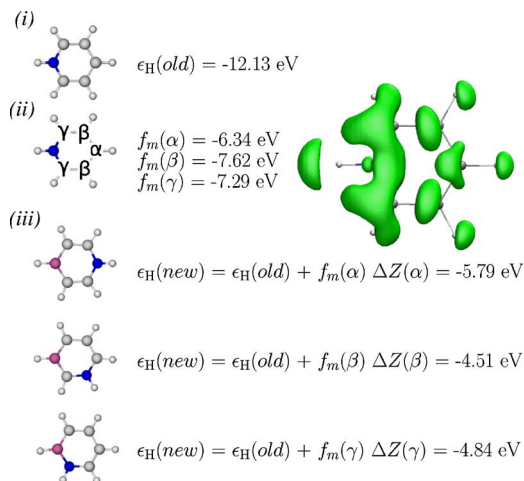


FIG. 2. Example of the employed procedure to predict changes in HOMO eigenvalues due to doping: (i) obtain $\epsilon_H(\text{old})$ from the self-consistent field KS-DFT calculation for $\text{B}_{n'=0}\text{C}_5\text{H}_6\text{N}_{n''=1}^+$; (ii) perform a finite difference calculation of the molecular Fukui function $\{f_m(\mathbf{R}_I)\}$ according to Eq. (8) at each nuclear site \mathbf{R}_I . The green isosurface illustrates the spatial distribution of the molecular Fukui function for a cutoff value of 6.34 eV at which the α site is dissected; and (iii) calculate the predicted $\epsilon_H(\text{new})$ after doping according to Eq. (9).

$\partial_{n_i} E[N_e, Z] = \epsilon_i$, one can relate the HOMO eigenvalue ϵ_H to the electronic chemical potential, $\mu_e = \partial_{N_e} E = \partial_{n_H} E = \epsilon_H$.

$\mu_n(\mathbf{r})$, on the other hand, can be identified as the functional derivative, $\delta E / \delta Z(\mathbf{r})$,

$$\mu_n(\mathbf{r}) = V_{\text{ESP}}(\mathbf{r}) = \int d\mathbf{r}' \frac{Z(\mathbf{r}') \text{erf}(\sigma|\mathbf{r} - \mathbf{r}'|) - \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (5)$$

which corresponds to a modified electrostatic potential of the proton and electron distributions, $Z(\mathbf{r})$ and $\rho(\mathbf{r})$, respectively, excluding “intranuclear” proton-proton Coulomb repulsion.

Now, using a Maxwell relation and in analogy to the conventional and nuclear Fukui functions, $f_c(\mathbf{r}) = \delta_{v(\mathbf{r})} \mu_e$ and $\{f_n(\mathbf{R}_I) = \partial_{R_I} \mu_e\}$, respectively,^{21,23,24} a molecular Fukui function, $f_m(\mathbf{r})$, can be defined as the mixed second order derivative of the total potential energy with respect to $Z(\mathbf{r})$ and electron number N_e ,

$$f_m(\mathbf{r}) = \frac{\partial \mu_n(\mathbf{r})}{\partial N_e} = \frac{\delta \mu_e}{\delta Z(\mathbf{r})} = \frac{\partial}{\partial N_e} \frac{\delta}{\delta Z(\mathbf{r})} E. \quad (6)$$

Exchanging the order of differentiation for the functional and partial derivatives in Eq. (6) (see Ref. 7), the molecular Fukui function equates the derivative of the modified electrostatic potential V_{ESP} with respect to N_e , to the variation of the HOMO eigenvalue ϵ_H with respect to the change in $Z(\mathbf{r})$,

$$f_m(\mathbf{r}) = \frac{\partial V_{\text{ESP}}(\mathbf{r})}{\partial N_e} = \frac{\delta \epsilon_H}{\delta Z(\mathbf{r})}. \quad (7)$$

Equation (7) provides a direct way of predicting the change in the HOMO eigenvalue ϵ_H due to variation of $Z(\mathbf{r})$ at any given \mathbf{r} in the molecule through a single evaluation of the change in electrostatic potential due to a small variation of the HOMO's occupation number by Δn_H . To this end, we calculate the left-hand side derivative in Eq. (7) by slightly decreasing the HOMO occupation number. For all the

nuclear sites $\{\mathbf{R}_I\}$, the values of the molecular Fukui function $f_m(\mathbf{R}_I)$ represent the susceptibility of the HOMO eigenvalue due to variation of the atomic number $Z(\mathbf{R}_I)$ of nucleus I ,

$$f_m(\mathbf{R}_I) = \frac{V_{\text{ESP}}(\mathbf{R}_I, N_e + \Delta N_e) - V_{\text{ESP}}(\mathbf{R}_I, N_e)}{\Delta N_e}. \quad (8)$$

Note that in order to evaluate this derivative, fractional particle numbers shall be used, which is perfectly valid as far as reversible changes of state functions are concerned: they can be seen as points on arbitrary but reversible paths connecting two real systems. However, they do lack a realistic correspondence in chemical space and are consequently irrelevant if the connecting path is irrelevant. We refer to Ref. 7 for a more in-depth discussion of this aspect.

The change in the HOMO eigenvalue can then be estimated from the right-hand side part in Eq. (7),

$$\epsilon_H[Z(\mathbf{r}) + \Delta Z] = \epsilon_H[Z(\mathbf{r})] + \sum_I f_m(\mathbf{R}_I) \Delta Z_I, \quad (9)$$

where the sum goes over all atoms which shall be doped; $\Delta Z_I = \Delta Z(\mathbf{R}_I)$ is the variation of the atomic number through doping, $\Delta Z = \sum_I \Delta Z_I$. Here, we limit ourselves to $\Delta Z = 0, \pm 1$ and to changes which only lead to the atomic numbers corresponding to carbon, nitrogen, or boron.

C. Computational details

The BLYP-approximation^{25–27} to the Kohn-Sham exchange-correlation potential^{28,29} has been used together with the Goedecker pseudopotentials from Refs. 30–32, and a converged plane-wave basis. Geometries have been optimized for every doping step and before evaluating the new HOMO eigenvalues. Fractional occupation numbers have been imposed by using noninteger charges, a standard feature in the employed *ab initio* code, CPMD.³³

In order to evaluate Eq. (9), the HOMO occupation number has been reduced in Eq. (8) from $n_H = 2$ to 1.98, such that $\Delta N_e = \Delta n_H = 0.02$, and the electronic singlet spin multiplicity has been kept constant for all cases. Furthermore, errors due to the employed approximated exchange-correlation potential, such as an increasing self-interaction error for fractional occupation number,³⁴ or due to the use of pseudopotentials have been neglected.

Figure 2 exemplifies the procedure of how to apply Eq. (9) to $\text{B}_{n'=0}\text{C}_5\text{N}_{n''=1}\text{H}_6^+$ in order to obtain the predicted change in ϵ_H due to the doping leading to any of the three possible mutants with the stoichiometry $\text{B}_{n'=1}\text{C}_4\text{N}_{n''=1}\text{H}_6$ (see also Fig. 1).

Firstly, the KS-DFT HOMO eigenvalue ($\epsilon_H[Z(\mathbf{r})]$) in Eq. (9) is calculated for C_5NH_6^+ . Secondly, the molecular Fukui function, i.e., the change in the electrostatic potential due to a slight variation in HOMO occupation number, $\Delta n_H = 0.02$, is computed for the same compound [Eq. (8)] at each atomic site. Finally, using Eq. (9), HOMO eigenvalues of the three mutants after an additional boron doping are predicted. ΔZ is always equal to -1 in this example, i.e., the atomic number decreases by one when substituting a carbon nucleus by a boron.

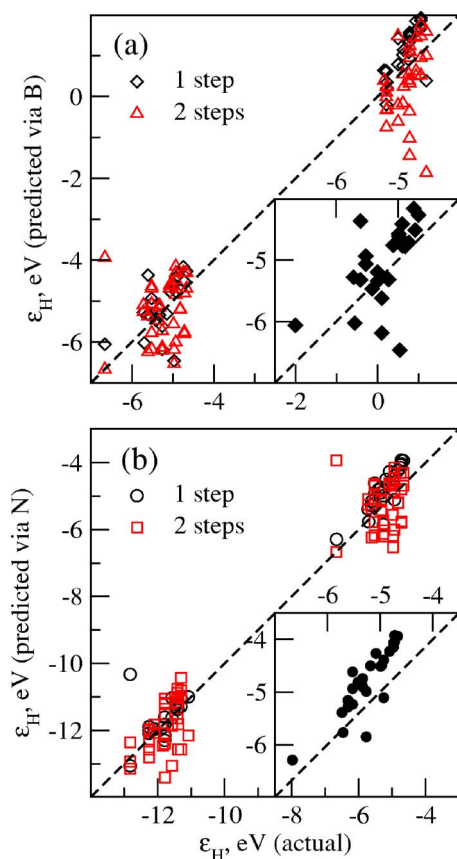


FIG. 3. Correlation between predicted HOMO eigenvalues from Eq. (9) with actually computed values. (a) anionic B-doped intermediates ($\epsilon_H \approx 1$ eV); (b) cationic N-doped intermediates ($\epsilon_H \approx -12$ eV).

III. RESULTS AND DISCUSSION

A. Accuracy of the predicted changes

In order to assess the accuracy of the predicted HOMO eigenvalues, actual KS-DFT eigenvalues have also been calculated for all the mutants and compared to the predicted ones. Evaluating the derivatives of the electrostatic potential we set ΔN_e to be small (0.02). In this case Eq. (7) is practically exact. The change in the HOMO eigenvalue, however, is predicted for relatively large changes in Z_I , $\Delta Z_I = \pm 1$. This error, introduced by the finite difference, can be evaluated for each mutant through direct comparison of the predicted and

calculated HOMO eigenvalues. Of course, this is only feasible because of the limited number of possible mutants.

Figure 3 shows the correlation between predicted and actual (calculated with the standard KS-DFT self-consistent field procedure) HOMO eigenvalues. The change in the HOMO eigenvalue due to doping can be estimated via cationic or anionic intermediates, which we refer to as a *one-step* prediction. It is also possible to skip the charged intermediates and change two atomic numbers simultaneously (with opposite signs). This of course yields only neutral intermediates and is denoted as a *two-step* prediction. The insets in Fig. 3 feature the correlation for the neutrally doped species only; however, the estimations were done using both one- and two-step predictions.

Root mean square deviations of the HOMO values of the neutral systems indicate that there is a systematic shift of the correlation for those results involving the cationic N-doped intermediates. This difference in accuracy might be a consequence of the fact that anionic systems are frequently less accurately described by conventional generalized gradient approximations than cationic systems.³⁵ For the correlation resulting from the use of anionic B-doped intermediates, no systematic shift has been found. Apart from the employed large changes in Z_I the difference in the correlation might also be due to the employed pseudopotentials. A quantitative analysis of these contributions is a work in progress.

Overall, the correlation between the predicted and calculated HOMO eigenvalues is good. This implies that the change in electronic eigenvalues due to doping can be predicted with reasonable accuracy and without evaluation of the actual eigenvalue corresponding to the doped mutant.

B. Doping pathways

Table I summarizes all the actual HOMO eigenvalues corresponding to the structures in Fig. 1, which are correlated with the predicted values in Fig. 3. The table shows that the [BNBNBN] isomer has the globally lowest eigenvalue, -6.66 eV (predicted values -6.29 eV via N or -6.06 eV via B). The highest eigenvalue is exhibited by the [CBNCBN] mutant, -4.67 eV (predicted -3.94 eV via N doping, or -4.27 eV via B doping).

For the rational design search of an optimized compound

TABLE I. HOMO eigenvalues in eV for all the isoelectronic mutants as defined in Fig. 1. Each column contains all the structural isomers for a given stoichiometry and charge as defined by the label (n', n'').

(0,0)	(1,0)/(0,1)	(1,1)	(2,1)/(1,2)	(2,2)	(3,2)/(2,3)	(3,3)
-6.07	-12.13/0.40	-5.70	-11.57/0.62	-4.67	-12.82/0.50	-6.66
		-5.18	-11.79/0.23	-4.97	-11.30/0.78	-5.52
		-5.42	-12.11/0.76	-4.72	-11.79/0.21	-4.93
			-11.42/0.79	-5.61	-12.26/0.94	
			-11.08/0.16	-5.33	-11.39/1.19	
			-11.85/0.64	-4.99	-11.41/1.06	
				-4.82		
				-5.26		
				-4.74		
				-5.72		
				-5.08		

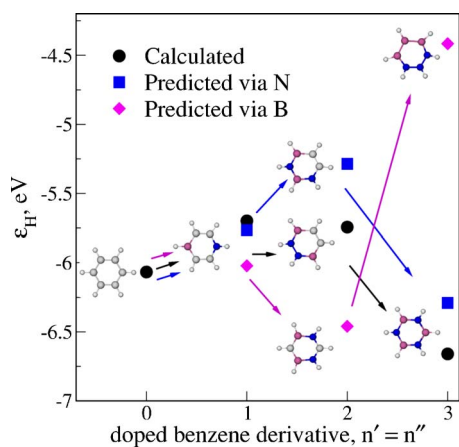


FIG. 4. Pathways of the steepest descent algorithm for minimizing ϵ_H : via N-doped cationic intermediates (squares); via B-doped anionic intermediates (diamonds). Circles show the globally minimal path for actually calculated ϵ_H values.

(e.g., with maximal/minimal HOMO eigenvalue), the predictions of the eigenvalues based on gradients (Fukui function) shall be combined with an optimization or transition-path searching algorithm. In the case of benzene, even the steepest descent algorithm, which uses neither backward moves nor bookkeeping, is capable of finding the compound with the lowest/highest HOMO value. In order to illustrate this, the “doping paths” corresponding to the steepest descent in HOMO values, are displayed in Fig. 4. Here, the change in the minimal eigenvalue with the progressive doping (increasing values of $n' = n''$ from left to right in Fig. 1) is shown. The choice of this coordinate is as arbitrary as the initial value for $n' = n''$. The actual values correspond to sampling of all possible mutants, for which the complete set of actual HOMO eigenvalues is needed. This is the most inefficient approach but it ensures the globally optimal path.

Figure 4 shows that the one step series of cationic N-doped intermediates visits other mutants than the optimal path, but still leads to the correct, globally optimal, compound [BNBNBN]. The pathway containing only anionic B-doped intermediates does not lead to the optimal compound but is trapped in a local minimum. This exemplifies the fact that the chemical space “energy” (ϵ_H) landscape is high dimensional with many local minima. Together with the imposed “prohibition” of backward moves (i.e., dedoping of the systems and choosing an alternative path), this indicates the need for more sophisticated algorithms for finding efficient transition paths. Such algorithms are already available³⁶ and can easily be merged with our approach.

C. Conclusion

In summary, using benzene and its BN-doped derivatives as test case systems, we have demonstrated that the molecular grand-canonical ensemble density functional theory can significantly improve the efficiency of rational compound design approaches towards B- and N-doped conjugated materials. This approach promises that an enhancement of efficiency can be achieved in comparison to the screening of the entire chemical space. A significant impact is expected on the

in silico design of compounds derived from larger molecules such as hexabenzocoronene or pentacene, which is work in progress.

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