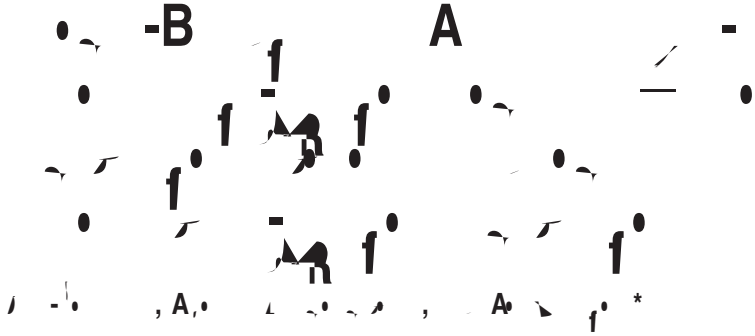

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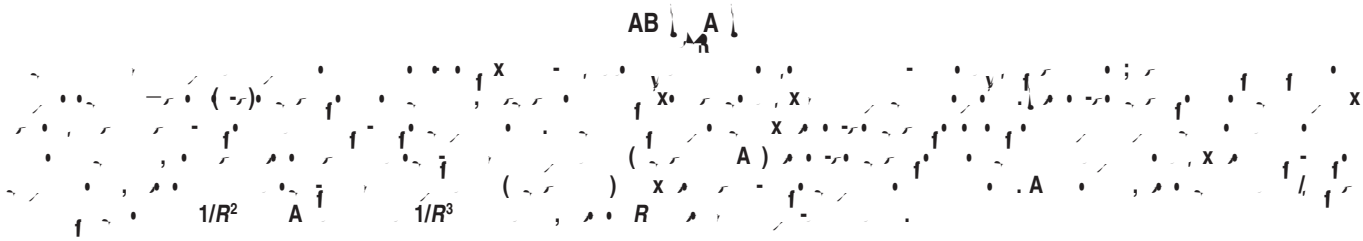

and indirect bandgap Si quantum dots and explain how the balance between LR and SR exchange interactions affects the size dependence of Δ_X.

LUMO can be a_1, e, or t_2 depending on the size of the dot.[2] The spin−orbit interaction splits t_2 into $\Gamma_8 + \Gamma_7$, t_1 into $\Gamma_8 + \Gamma_6$, and transforms e into Γ_8 and a_1 into Γ_6.[26] The calculated energy level diagrams (including spin−orbit interaction) are shown in Figure 1 column (i) for two cases: (a) InAs direct-gap quantum dots where the dot HOMO has the $\bar{\Gamma}_{8v}(\Gamma_{8v})$ symmetry and the LUMO has the $\bar{\Gamma}_{6c}(\Gamma_{6c})$ symmetry, leading to $\Gamma_8 \otimes \Gamma_6 = \Gamma_3 + \Gamma_4 + \Gamma_5$ excitons. (b) Si indirect-gap quantum dots with $\bar{\Gamma}_{8v}(\Gamma_{8v})$ HOMO and $\bar{\Gamma}_{8c}(X_{6c})$ LUMO (in our calculations the $\bar{\Gamma}_{8c}$ state is always below the $\bar{\Gamma}_{6c}$ state), leading to $\Gamma_8 \otimes \Gamma_8 = \Gamma_1 + \Gamma_2 + \Gamma_3 + 2\Gamma_4 + 2\Gamma_5$ excitons. Here the label in parentheses is the bulk state that folds into the dot state indicated by an overbar. Column (ii) in Figure 1 shows how the HOMO and LUMO single-particle states produce an exciton state due to direct e-h Coulomb interaction, but neglecting as yet all e-h exchange interactions. Column (iii) shows how the levels split due to the inclusion of all e-h Coulomb and exchange integrals. We define Δ_X as the energy separation between the lowest dark CI state (dotted line) and lowest bright CI state (solid line). The dark/bright character of the exciton states is determined by their dipole matrix elements with respect to the ground state. Although the Γ_5 symmetry is optically allowed, we find that the lower-energy Γ_5 excitons of Si dots have oscillator strength 3 orders of magnitude smaller than that of the higher-energy Γ_5 excitons, so we determine that only the higher-energy 3-fold Γ_5 excitons are bright.

To examine the magnitude of the SR and LR contributions, we calculate Δ_{coul} and Δ_X using the artificial step-function

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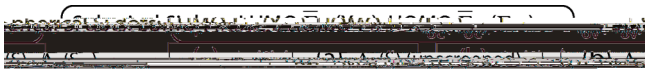

. . Same as Figure 2 but for indirect-gap spherical Si quantum dots. The red triangles denote the peak of $\Delta_X(S)$.

The origin of the HOMO and LUMO states can be determined by calculating the decomposition of the dot orbitals into bulk Bloch states throughout the Brillouin zone[27]

$$\psi_{(i)}^{dot}(\quad) = \sum_{n,} C_{n,}^{(i)} u_{n,}(\quad) e^{i\ \sim} \tag{8}$$

Figure 4 shows this decomposition for spherical InAs and Si dots of radius $R = 15$ Å, clearly showing that the LUMO state of the InAs dot is a Γ-like state (98.2% derived from the bulk Bloch states around Γ), whereas the LUMO state of the Si dot is an *X*-like state (99.7% derived from the bulk Bloch states around *X*).

The correlation between the range of the exchange interaction and the direct/indirect character of the band gap can be understood based on the microscopic origin of the LR and SR exchange interactions. As shown in ref 8, the LR part of the e-h exchange interaction in quantum dots originates primarily from monopole−monopole interactions between transition charges located in each unit cell of the underlying bulk lattice. The exchange integral $K_{VC,VC}$ between the HOMO wave function (*V*) and the LUMO wave function (*C*) can be written as[8]

$$K_{VC,VC} = \sum_{m\neq n}^{N} \iint \frac{\chi_m^*(\quad_1)\chi_n(\quad_2)}{\bar{\varepsilon}(\quad_1,\quad_2)|\quad_1 - \quad_2|} d\quad_1 d\quad_2 \tag{9}$$

where

$$\chi_m(\quad) = \sum_{\sigma} \psi_V(\quad,\sigma)\psi_C^*(\quad,\sigma) \tag{10}$$

if $\quad$ is in the eight-atom unit cell Ω_m and 0 otherwise, and the sum runs over the primitive cells contained in the quantum dot. The LR monopole−monopole contribution to $K_{VC,VC}$ is

$$K_{VC,VC}^{M-M} = \sum_{m\neq n}^{N} \frac{q_m^* q_n}{\bar{\varepsilon}(\quad_m - \quad_n)|\quad_m - \quad_n|} \tag{11}$$

where $q_n = \int \chi_n(\quad) d\quad$ is the transition charge in the unit cell Ω_n located at $\quad_n$. The monopole-monopole term exists because the electron and hole envelope functions are not constant inside each bulk-like unit cell. If they were, then $q_n \equiv 0$ (at least in the single-band effective mass approximation) because of the orthogonality of the bulk LUMO and HOMO Bloch functions. By Taylor expanding the hole and electron envelope functions in each unit cell *n*, we find that

. . Real space (RS) wave function square and majority representation (MR) decomposition of single-particle (a) LUMO $\bar{\Gamma}_{6c}(\Gamma_{6c})$ and (b) HOMO $\bar{\Gamma}_{8v}(\Gamma_{8v})$ states for spherical InAs, and (c) LUMO $\bar{\Gamma}_{8c}(X_{6c})$ and (d) HOMO $\bar{\Gamma}_{8v}(\Gamma_{8v})$ states for spherical Si dot, respectively, with dot radius of $R = 15$ Å.

where $F_{V,C}(\ _n)$ are the HOMO and LUMO envelope functions, respectively, and $\_{}_{V,C} = \langle \psi_V | \_{} | \psi_C \rangle$ is the dipole matrix element between the bulk HOMO and LUMO Bloch functions. Thus, the lowest-order nonvanishing contribution to the transition charge q_n is proportional to the dipole matrix element $\_{}_{V,C}$

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